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XXXI.—SOME NEW DERIVATIVES OF SECONDARY BUTYL ALCOHOL.

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The source of the compounds which have been prepared was the so-called "oil of acetone" or "methylethyl ketone," which has recently been put upon the market as a commercial solvent. We were unable to find out from what substances the oil was prepared, but it is apparently identical with the French product described by Buisine,[1] which is made by the dry distillation of the calcium salts of the fatty acids obtained from wool-washings. The commercial oil contains about 60 per cent by volume of methylethyl ketone, which can be readily separated by fractionation. It seemed that the reduction of this ketone might offer a convenient method for obtaining secondary butyl alcohol, which has heretofore been prepared chiefly from its iodide, obtained by the action of hydriodic acid upon erythrite. We hoped to obtain the secondary alcohol in quantities sufficient for the preparation of the simple derivatives, of which very few are known, and for a study of the relations of the secondary butyl compounds to the

[1] A. and P. Buisine: Compt. rend., 126, 351.

isomeric normal, iso, and tertiary derivatives. As a large supply of the commercial oil was available, we made an extended study of the action of various reducing agents upon the ketone. No detailed comparative experiments on the reduction of fatty ketones have been reported in the literature, and it seemed of interest to determine under what conditions the reduction is most readily effected.

The ketone was subjected to reducing agents in acid, neutral, and alkaline solution. The literature relating to the reduction of fatty ketones by acid agents is very scanty. The experiments of Bogdanowska[1] show that dibenzyl ketone is not reduced when treated with zinc and strong acids; the secondary alcohol was readily obtained, however, by the use of hydriodic acid and phosphorus. According to Bielohoubek,[1] methylpropyl ketone yields no alcohol on treatment with acid reducing agents; and, finally, Lachowitz[3] has shown that by the action of acids on iron or zinc the halogen can be easily removed from chlor ketones while the carbonyl group remains intact. On the other hand, the diketones, diacetyl (butadione), and acetylpropionyl (pentadione-2,3) yield ketols with zinc and dilute sulphuric acid; and, as Combs[4] has shown, acetylacetone (pentadione-2,4) is reduced to the corresponding glycol most readily by sodium amalgam in the presence of free hydrochloric or acetic acids. Further, it is well known that fatty aldehydes and aromatic ketones yield more or less readily to acid reducing agents. In view of these diverse results, we undertook a careful study of the action of acid reducing agents upon methylethyl ketone. Our results confirm those obtained by former workers on simple fatty ketones. All attempts to reduce the compound to secondary butyl alcohol by the action of hot or cold mineral and organic acids on zinc or iron were unsuccessful.

Attempts to reduce the ketone in neutral solution were also unsuccessful. Aluminum amalgam, which has been shown by Wislicenus[5] to be very efficient for the reduction of aro-

[1] Ber. d. chem. Ges., **25**, 1272.
[2] *Ibid.*, **9**, 925.
[3] *Ibid.*, **17**, 1162.
[4] Ann. chim. phys., (6), **12**, 228.
[5] J. prakt. Chem., **54**, 46.

matic ketones, gave negative results; no secondary alcohol could be obtained, though several experiments were made under varying conditions.

Reduction in alkaline solution was the only method which yielded the secondary alcohol. Sodium amalgam gave a yield of from 30 to 50 per cent of the theoretical quantity according to the conditions of treatment. The reduction required from one to two weeks for completion, and hence the process is inconvenient. As zinc and alcoholic potash gave excellent results as applied by Zagoumenny[1] to aromatic ketones, we attempted to reduce methylethyl ketone with this agent. Our results were unsatisfactory; in one experiment no secondary alcohol was formed; in another, under slightly different conditions, the yield was 4 per cent of the theoretical quantity. High-boiling condensation-products, doubtless analogous to those given by dibenzyl ketone,[2] were formed.

As it seemed probable that the action of aluminium and caustic soda upon the ketone might be analogous to that of sodium amalgam, we studied the effect of this reagent. Aluminium shavings were mixed with aqueous solutions of the ketone, and a concentrated solution of caustic soda then added gradually in small quantities. The alkali slowly threw the ketone out of solution, but, notwithstanding this fact, there resulted, in one experiment, a yield of 31 per cent of the theoretical quantity of secondary alcohol. When dilute alcohol was used as a solvent to keep the ketone in solution, no secondary alcohol was obtained, even after prolonged treatment with the reducing agent. The application of aluminium and caustic soda as a reducing agent will be further studied in this laboratory.

The action of sodium upon solutions of the ketone in methyl alcohol and in boiling amyl alcohol gave unsatisfactory results. Traces only of the secondary alcohol were formed, together with considerable quantities of high-boiling condensation-products.

Electrolytic hydrogen also gave poor results. The best

[1] Ann. Chem. (Liebig), 184, 175.
[2] Bogdanowska: Ber. d. chem. Ges., 25, 1272.

yields were obtained with a current of from 1 to 2 amperes and half-normal caustic soda as the electrolyte, while the solutions were cooled by means of a water-jacket. Under these conditions 16 per cent of the theoretical yield of the secondary alcohol, with some dimethyl pinacone, were obtained in thirty-six hours.

The action of sodium upon moist ethereal solutions of the ketone was found by far the most efficient process for reduction. We followed, in general, the method used by Rohn[1] for reducing methylisoamyl ketone, and by Wislicenus[2] for the reduction of methyl-β-butyl ketone. The ketone was dissolved in ether, floated over water in a flask attached to a reflux condenser, and reduced by the gradual addition of sodium in small chips. The process required from seven to eight days and gave a yield of about 50 per cent of the calculated quantity of secondary alcohol with about 15 per cent of dimethyl pinacone. When the ethereal solution was over a strong solution of sodium bicarbonate, as recommended by Bogdanowska,[3] in place of water, there was no increase in the yield of alcohol. When the reaction was carried out at the temperature of melting ice the yield of the secondary alcohol was increased to 74 per cent and the time required was reduced to four days.

The above results indicate that methylethyl ketone cannot be reduced to secondary butyl alcohol by acid or neutral agents. Alkaline reagents yield the alcohol in varying amounts up to 74 per cent of the calculated quantity. At high temperatures high-boiling condensation-products are formed; at low temperatures the products are limited to secondary alcohol and dimethyl pinacone. The use of alcoholic solvents seems to be detrimental. Of the twelve agents studied, metallic sodium applied to a cooled, moist ethereal solution of the ketone was by far the most efficient.

The boiling-points of secondary butyl alcohol given in the literature, range from 96° to 100°, and the specific gravities at 0° from 0.827 to 0.850. Careful purification of our product with

[1] Ann. Chem. (Liebig), **190**, 309.
[2] *Ibid.*, **219**, 309.
[3] Ber. d. chem. Ges., **25**, 1272.

sodium, followed by repeated fractionation, resulted in a considerable quantity of the secondary alcohol boiling constantly at 99°.7 to 99°.9 (corr.) at 756 mm. pressure. This determination agrees very closely with that reported by Lieben,[1] who found the boiling-point to be 99° at 738 mm. The specific gravity of our preparation was 0.8078 at $\frac{20°}{4°}$, 0.8223 at $\frac{0°}{4°}$. Lieben gives the numbers 0.81 at 22°, 0.827 at 0°. The high values reported by other observers may perhaps be due to incomplete elimination of the halogen compounds involved in the preparation of the alcohol.

As the secondary alcohol contains an asymmetric carbon atom, attempts were made to split the compound up into optically active substances by the action of various micro-organisms upon dilute solutions of varying strength at varying temperatures. In no case was an optically active substance obtained.

Secondary butyl chloride was readily obtained by passing dry hydrogen chloride through a boiling mixture of the secondary alcohol and zinc chloride, and by the action of phosphorus trichloride on the alcohol. The former method proved much more efficient than the latter. According to Malbot and Gentil[2] the use of zinc chloride is of no advantage in the preparation of the halides of higher homologues of ethyl alcohol. Our experiments, however, show that this statement does not hold good in the case of secondary butyl chloride; for when the zinc salt was omitted we could in no case get any secondary chloride by the action of hydrogen chloride at ordinary pressures. Estreicher,[3] however, whose paper appeared during the course of our work, obtained the halide by heating in sealed tubes solutions of hydrogen chloride in the secondary alcohol saturated at 0°.

Secondary butyl bromide, which was hitherto known[4] only in an impure state, we readily obtained in quantity by the action of phosphorus tribromide on the secondary alcohol. The alkyl bromide was not formed when dry hydrogen bromide

[1] Ann. Chem. (Liebig), **150**, 114
[2] Ann. chim. phys., (6), **19**, 405.
[3] Ber. d. chem. Ges., **33**, 438.
[4] Meyer and Müller: J. prakt. Chem., **46**, 183.

was led through a boiling mixture of the secondary alcohol and zinc chloride, although by this treatment small amounts of the secondary chloride were obtained.

Secondary butyl esters resulted from the action of acyl chlorides on the secondary alcohol. The acetic ester was the only one hitherto known. It is readily formed by the action of acetyl chloride and of a mixture of sulphuric and acetic acids upon the alcohol. The propionic and isovalerianic esters were prepared from the acid chlorides in an analogous way. Disecondary butyl succinic ester resulted when the secondary alcohol (1 mol.) was heated with succinyl chloride (1.2 mol.) although under these conditions the formation of the acid ester would be expected. The only products of the reaction were the neutral ester and succinic anhydride; the latter separated out in considerable quantity as the mixture cooled.

Attempts to obtain the benzoic ester by the Baumann-Schotten reaction resulted unsatisfactorily; and no ester was formed by leading dry hydrogen chloride through a boiling solution of benzoic acid in the secondary alcohol. It was readily obtained, however, by heating the alcohol with benzoyl chloride for some time.

By the fractionation of the high-boiling residue left from the rectification of the secondary butyl alcohol, we obtained the dimethyl pinacone (dimethyl-3,4-hexandiol-3,4) prepared by Lawrinowics[1] by the action of sodium amalgam upon methylethyl ketone. Zelinsky and Krapivin[2] consider this compound to exist in two stereoisomeric forms: a solid crystalline modification melting at 49°.5, and a liquid boiling at 200°–205°. They have found both forms to be of the same composition. The presence of two asymmetric carbon atoms is the basis of this view. Schram[3] has shown that both products have the same boiling-point. By repeated fractionation of our product we obtained the substance in a nearly pure state, boiling at 205° to 205°.7 (corr.). On cooling, white crystals separated which melted at 49°. Recrystallization

[1] Ann. Chem. (Liebig), 183, 124.
[2] J. Chem. Soc. (London), 64, 1, 390 (abstracts).
[3] Ber. d. chem. Ges., 16, 1582.

from alcohol did not change the melting-point. A careful study of the properties of the crystals and the liquid from which they separated leads us to the view that the two products are not isomers but are the same substance. A mere trace of impurity probably prevents dimethyl pinacone from assuming the crystalline form. Liquid diisobutyl pinacone, as shown by Rohn,[1] crystallizes with great difficulty. Both the crystals and the liquid obtained by us were inactive to polarized light. Attempts to convert the dimethyl pinacone into dimethyl-3,4-dibrom-3,4-hexane, and to obtain subsequently from this a new octane were rendered futile by the difficulty of preparing the dibromide of the glycol in a pure state. No solid dibromide analogous to that obtained from ordinary pinacone by Pawlow[2] and by von Baeyer[3] could be isolated. Our product was an unstable oil which decomposed on distillation under reduced pressure.

By the action of sodium on secondary butyl bromide we obtained disecondarybutyl, one of the eighteen possible isomeric octanes, of which three were previously known: normal octane (b. p. 125°), diisobutyl (b. p. 109°), and hexamethylethane (b. p. 105° to 106°). Pure dry secondary butyl bromide is not affected by sodium even when boiled with the metal; a solution of the bromide in perfectly anhydrous ether was unaffected by standing over sodium for eight days. Reaction sets in, however, when the ether or the bromide is not wholly dry, as has already been shown by Silva[4] in the case of isopropyl bromide. Slight additions of ethyl acetate greatly hastened the reaction without, however, increasing the yield of octane. As is usual, a blue solid formed an intermediate product in the reaction. This decomposed when warmed gently, lost its color, and gave off disecondarybutyl. No hydrocarbon was formed until the blue compound was decomposed; and none was obtained by extracting the blue substance with ether. The composition and decomposition of this blue product will be further investigated. After distill-

[1] Ann. Chem. (Liebig), **190**, 311.
[2] *Ibid.*, **196**, 124.
[3] Ber. d. chem. Ges., **26**, 2563.
[4] *Ibid.*, **8**, 948.

ing off the octane, the residual sodium still contained much organic matter, which accounts for the low yields of octane which were obtained. No gaseous products were evolved during the synthesis. Continued fractionation of the hydrocarbon failed to remove all of the halogen; even repeated distillation over sodium was ineffectual in this, although the octane had a nearly constant boiling-point. To get a halogen-free product, the crude octane resulting from a number of preparations was reduced first in a moist ethereal solution by sodium, then by the action of zinc on hydrochloric acid. The product, when washed with water and caustic potash, and fractionated, was completely free from halogen. About 0.5 gram, heated to 200° for two hours in a sealed tube with fuming nitric acid and silver nitrate, gave no indication of halogen.

Disecondarybutyl boils at 116° to 116°.2 at 750 mm. pressure and has a specific gravity of 0.7332 at $\frac{0°}{4°}$. The high specific gravity of the substance is remarkable, for it is even higher than that of normal octane. This relation, however, is in agreement with that recently shown by Young and Fortey[1] to exist between diisopropyl and normal hexane. The following table shows the relation of disecondary butyl to its isomers, normal octane, and diisobutyl:

	B. p.	Sp. gr. at $\frac{t°}{4°}$.
Normal octane, $CH_3—CH_2—(CH_2)_4—CH_2—CH_3$	125°	0.7184
Diisobutyl, $(CH_3)_2CH—(CH_2)_2—CH(CH_3)_2$	109.°2	0.7102
Disecondary butyl, $(CH_3)_2CH—CH(CH_3)_2$ $CH_3—CH_2$ $\quad$ $CH_2—CH_3$	116°–116°.2	0.7332

A comparison of the constants of the simple secondary butyl derivatives above noted with the constants of the isomeric normal, iso, and tertiary butyl compounds, shows that the boiling-points of the secondary derivatives lie near to,

[1] J. Chem. Soc. (London), 77, 1127.

but slightly lower than, the boiling-points of the isobutyl compounds; and with the exception of the alcohols and the succinic esters, the specific gravities in the two series bear the same relation. It would be expected, therefore, by analogy, that the boiling-point and specific gravity of disecondary butyl would be somewhat lower than the respective constants of diisobutyl. This, however, is not the case, for the relations are reversed, and disecondary butyl has the higher constants. It is interesting to note in this connection that propyl bromide has a greater specific gravity than has isopropyl bromide, yet dipropyl has a smaller specific gravity than has diisopropyl. The relations here are thus analogous to those existing between the isobutyl and secondary butyl derivatives. Further, it is interesting to note that the relations existing between the three octanes—normal octane, diisobutyl, and disecondary butyl,—as shown above, are precisely the same as regards both boiling-points and specific gravities as exist between the three isomeric decanes of analogous structure—normal decane, diisoamyl, and active diamyl, respectively.

By the nitration of disecondary butyl with fuming nitric acid at 100°, a tertiary nitro compound was obtained in small quantity.

EXPERIMENTAL PART.

Reduction of Methylethyl Ketone.

The crude commercial oil was dried over potassium carbonate and fractionated by means of a tower 70 centimeters high filled with glass, as proposed by Hempel.[1] Five fractionations served to collect a large portion of the liquid in a fraction boiling at 79° to 82°; most of the residue boiled at 93° to 110°. The lower fraction had all the properties of methylethyl ketone; 750 cc. of the crude oil gave 420 cc. of the ketone, equivalent to 56 per cent by volume. The ketone was soluble in about 8 parts of water, readily soluble in dilute acids, but nearly insoluble in solutions of the alkali hydroxides. As there has been no systematic study of the reduction of a fatty

[1] Ztschr. anal. Chem., **20**, 502.

ketone, we studied carefully the action of 12 reducing agents upon this ketone, and the results are given in some detail, as they are a contribution to laboratory practice which may prove of value.

Reduction in Acid Solution.

Zinc and Glacial Acetic Acid.—The method of Krafft[1] for the reduction of higher fatty aldehydes was followed: 72 grams of the ketone, dissolved in 500 grams of glacial acetic acid, were boiled under a reflux condenser for a week with 225 grams of zinc dust—three and a half times the calculated quantity. Half the zinc was added at first, the remainder after three days. The product was made alkaline with caustic soda and shaken with ether. The ethereal solution, when dried over potassium carbonate and rectified, left a residue which boiled at 76° to 83°; it was unchanged ketone (b. p. 81°). Repetition gave a similar result.

Zinc and Dilute Sulphuric Acid.—Thirty grams of the ketone were dissolved in 300 cc. of water in a flask attached to an air condenser; 80 grams of zinc dust were added, and dilute sulphuric acid was poured in at intervals. The zinc sulphate formed gradually threw the ketone out of solution, and more water was added. After two days the zinc had almost all dissolved. The product was extracted with ether, and the extract dried over potassium carbonate and rectified. The residue, after removal of the ether, boiled at 76° to 83° and weighed 12 grams. It was unchanged ketone. No secondary alcohol was formed in the process. Other experiments resulted similarly. The great loss of ketone which occurred in this and also in the preceding experiment may possibly be due to complete reduction of the ketone to a hydrocarbon; for the work of Rötering and Zincke[2] on the reduction of ketonic acids to oxy-acids has shown that in this case there is often much loss due to the formation of hydro acids.

Iron and Acetic Acid.—Fifty grams of the ketone, dissolved in 360 grams of 50 per cent acetic acid, were heated gently on

[1] Ber. d. chem. Ges., 16, 1715.
[2] *Ibid.*, 9, 313.

the water-bath under a reflux condenser with 77 grams of iron filings—twice the weight theoretically necessary. After twelve hours the semi-solid product was diluted, made alkaline, and extracted with ether as described above. No secondary alcohol was obtained; the ethereal extract contained only unchanged ketone. As in the previous methods, much ketone was lost. A check experiment gave similar results.

Iron and Hydrochloric Acid.—Fifty grams of the ketone were dissolved in 300 cc. of water in a flask provided with an air-condenser and immersed in cold water. Seventy-seven grams of iron filings were added and then concentrated hydrochloric acid at intervals. The cooling was continued for twelve hours, and the reaction then allowed to progress at the room temperature for two days. The ethereal extract of the neutralized product was dried and fractionated. It yielded only unchanged ketone. The loss of ketone was about 50 per cent. Repetition gave a similar result.

Reduction in Neutral Solution.

Aluminium Amalgam.—The reagent was prepared as directed by Wislicenus and Kaufmann[1] and was freshly made for each experiment. Twenty-five grams, or twice the calculated quantity of aluminium amalgam, were added to a solution of 50 grams of the ketone in a liter of water in a flask attached to a reflux condenser. The mixture was agitated frequently. The evolution of hydrogen was vigorous. After forty-eight hours the liquid was decanted off, saturated with soda, and extracted with ether. The dried extract all distilled over below 89°, nearly all at 78° to 85° after removal of the ether. It was unchanged ketone. Repetition of the process with 50 grams of the amalgam and four days' treatment, gave essentially the same results.

Reduction in Alkaline Solution.

Sodium Amalgam (WITH B. R. RICKARDS).—Aqueous solutions of the ketone were treated in the usual way with 3 per cent sodium amalgam. Twice the calculated quantity of the amalgam was necessary, and the process was very slow.

[1] Ber. d. chem. Ges., 28, 1323.

Frequent agitation and neutralization of the alkaline liquid hastened the reaction. With frequent shaking by hand, the time required was from seven to ten days, and the yield of secondary alcohol was 30 per cent of the calculated amount. With mechanical stirring the yield rose to 50 per cent, but the time required was fifteen days. The alcohol was obtained from the product by fractionation of the ethereal extract, which had been dried over potassium carbonate. In all the experiments with sodium amalgam some dimethyl pinacone also was formed.

Zinc and Alcoholic Potash.—We followed the process recommended by Zagoumenny[1] for the reduction of benzophenone. Fifty grams of the methylethyl ketone in 200 grams of methyl alcohol were mixed with fifty grams of powdered caustic potash; 75 grams of zinc dust were added and the mixture heated on a water-bath under a reflux condenser. Methyl alcohol was used, as it could subsequently be separated easily from any secondary butyl alcohol. The heating was continued for five hours. The ethereal extract of the diluted product was dried over potassium carbonate and distilled. It all came over below 85°; the product was unchanged ketone. In another experiment 75 grams of caustic soda and 110 grams of zinc were used, and the heating was continued for ten hours. The result was much unchanged ketone, 3 grams of crude secondary butyl alcohol boiling at 90° to 115°, and a small quantity of a liquid boiling at 190° to 250°. The yield of the crude alcohol was 4 per cent of the theoretical quantity. The high-boiling liquid was not obtained in sufficient quantity for study, but it is doubtless a condensation-product analogous to those obtained by Bogdanowska,[2] when reducing dibenzyl ketone by this agent.

Aluminium and Caustic Soda.—Fifty grams of the ketone in 500 cc. of water were mixed with 25 grams—twice the calculated amount—of aluminium shavings in a flask provided with a reflux condenser. Concentrated caustic soda solution was added at intervals through the condenser tube. Hydrogen

[1] Ann. Chem. (Liebig), 184, 175.
[2] Ber. d. chem. Ges., 25, 1272.

was evolved smoothly, and the action could be regulated by adding more or less alkali as the conditions required. As the mixture became more alkaline, the ketone separated partly from solution. After two days' treatment the oils were taken up with ether, dried, and fractionated. Sixteen grams of secondary butyl alcohol, boiling at 97° to 102°, and 27 grams of unchanged ketone were obtained, together with a small quantity of liquid which boiled above 102°. The yield of the secondary alcohol was 31 per cent of the theoretical amount. Experiments with dilute alcohol, as a solvent to prevent the separation of the ketone, resulted unsatisfactorily; no secondary alcohol was obtained by this treatment.

Electrolytic Hydrogen (WITH B. R. RICKARDS).—A porous cup containing half-normal caustic soda as electrolyte was immersed in a 12 per cent aqueous solution of the ketone, which was kept cold by running water. The anode was of platinum, the cathode of iron gauze. With a current of 1 to 2 amperes the yield of secondary alcohol, in thirty-six hours, reached 16 per cent of the theoretical amount. Other experiments, under varied conditions, resulted in lower yields. In all cases some dimethyl pinacone also was produced.

Sodium and Methyl Alcohol, and Boiling Amyl Alcohol.—Thirty-five grams of sodium were added in small quantities at intervals to 50 grams of the ketone dissolved in 275 grams of methyl alcohol. The reaction required three days for completion. The product was decomposed with ice-water and extracted with ether. The final products were methyl alcohol, unchanged ketone, and a small quantity of a liquid boiling above 250°. No secondary alcohol was obtained. Treatment of the ketone in boiling amyl alcohol with sodium according to Bamberger's[1] method, gave unsatisfactory results also. From 36 grams of the ketone were obtained a few drops only of secondary alcohol boiling at 92° to 110°; the main product was a viscid oil which boiled at 250° to 290°. It was not further studied.

Sodium and Moist Ether.—The best yields of secondary butyl alcohol were obtained by the following process: 72

[1] Ber. d. chem. Ges., **22**, 944.

grams of the ketone were dissolved in five times the volume of ether and floated over a liter of water in a flask attached to a reflux condenser. The mixture was kept cool by immersion in ice-water, and was shaken frequently during the reduction so that the ethereal layer should remain moist. Through the condenser 138 grams of sodium, in small pieces, were thrown in, in small quantities at a time—slowly at first, then more quickly as the reaction became less violent. The addition of the sodium required four days. The ethereal layer was then removed, dried over potassium carbonate, and fractionated. The yields of secondary butyl alcohol boiling at 97° to 102° ranged from 69 to 74 per cent of the theoretical quantity. The yields of dimethyl pinacone ranged from 11 to 14 per cent. With less than the stated amount of sodium, some ketone remained unreduced. When cooling was dispensed with, the yield of the secondary alcohol fell to about 50 per cent, and the time necessary was increased to from seven to eight days. When the reduction was carried out with no shaking the yield of the alcohol decreased about 10 per cent. The use of a strong solution of sodium bicarbonate, as recommended by Bogdanowska,[1] in place of water resulted in the formation of from 50 to 55 per cent of the secondary alcohol and from 11 to 14 per cent of dimethyl pinacone. The use of bicarbonate with simultaneous cooling gave similar results; but trouble was caused in this case by the crystallization of the sodium carbonate, which rendered the mixture below the ether nearly solid and delayed the action of the metal. It was necessary to use enough ether so that there was a layer at least 2 cm. deep; otherwise there is some danger of explosions owing to the expulsion of particles of metal which ignite above the ethereal layer. In one experiment, when a small quantity only of ether was used, the reaction-mixture exploded with extreme violence on the second day of reduction.

Secondary Butyl Derivatives.

Secondary Butyl Alcohol.—The crude alcohol obtained above was fractionated under a tower. The greater portion boiled

[1] Ber. d. chem. Ges., **33**, 1272.

at 99° to 100°; this portion was now cooled to 0° and some clean sodium added to it. After several hours the metal was removed and the liquid again fractionated. The greater part formed a fraction which boiled at 99°.7 to 99°.9 (corr.) at 756 mm. pressure. The final distillation was made over a fragment of sodium. The specific gravity of the alcohol was 0.8078 at $\frac{20°}{4°}$; 0.8226 at $\frac{0°}{4°}$. The alcohol was soluble in 8 parts of water at 20°, readily soluble in dilute acids, but nearly insoluble in strong solutions of the alkali carbonates and hydroxides. Sodium has almost no action upon it at 0°, very slow action at 15°, but decomposes it vigorously at 60°. Concentrated sulphuric acid decomposes it with charring when the mixture is not well cooled. Concentrated nitric acid decomposes it explosively. With solid potash and carbon disulphide it gives a white crystalline compound doubtless analogous to potassium xanthate.

Attempts to Obtain Optically Active Modifications of Secondary Butyl Alcohol (With B. R. Rickards).—Varying strengths of solutions of the secondary alcohol were submitted to the action of the following organisms: *Bacillus coli communis;* Lactic acid bacillus (Claflin); *Penicillium glaucum; Bacillus megatherium; Bacillus Topfii.* The tubes containing the cultures were subjected to various temperatures for several days. In all cases the solutions remained clear, no gas was evolved, and no acid was formed. No optically active substances were obtained.

Secondary Butyl Chloride.—Small yields were obtained by the action of phosphorus trichloride on the alcohol: 20 grams of the alcohol were heated to boiling in a flask attached to a reflux condenser, and 18 grams of phosphorus trichloride were then added, drop by drop, through the condenser. The mixture was boiled for two and a half hours. A yellow crust, which was found to be phosphorus, separated during the heating. The mixture was distilled into cold water. A light oil separated; this was washed with water and soda, and dried over calcium chloride. The product boiled at 65° to 69° and weighed 10 grams, 40 per cent of the theoretical amount. Repetitions of the process gave lower yields. Heating for less

than two and a half hours caused a decrease in the yields. When the trichloride and the alcohol, in the proportions given, were allowed to stand together for two days at the room temperature, the quantity of secondary chloride formed was 16 per cent. Much better yields were obtained by leading dry hydrogen chloride through a boiling mixture of the secondary alcohol and zinc chloride: 20 grams of the alcohol with 15 grams zinc chloride were treated with dry hydrogen chloride for two hours. The yield of secondary butyl chloride was 15 grams, 60 per cent of the calculated amount. The gaseous products of the reaction were led through bromine which, on subsequent treatment with soda, yielded 14 grams of crude β-butylene bromide. A repetition of the process resulted in a yield of 64 per cent of the alkyl halide and 12 grams of β-butylene bromide. When no zinc chloride was present, no secondary butyl chloride was formed even by prolonged exposure of the boiling alcohol to the hydrogen chloride.

That the low yield obtained by the use of phosphorus trichloride in the previous experiments was not due wholly to the dehydrating action of the reagent, is shown by the fact that from 20 grams of the secondary alcohol and 18 grams of phosphorus trichloride only 5 grams of β-butylene bromide were obtained by leading the gaseous products through bromine. The loss is due, doubtless, to the formation of complex phosphorus ethers.

Tne crude secondary butyl chloride was washed, dried, and fractionated. It boiled at 67°.3 to 67°.8 (corr.) at 767 mm. pressure, and had a specific gravity at $\frac{20}{4}°$ of 0.8707. With cold alcoholic silver nitrate, a precipitate began to form almost immediately. With aluminium chloride it evolved hydrogen chloride and formed a red oil, which was decomposed at once by water.

Secondary Butyl Bromide (WITH H. G. JOHNSON).—Thirty-six grams of phosphorus tribromide were slowly dropped into 20 grams of secondary butyl alcohol contained in a flask attached to a reflux condenser. The alcohol soon became hot, and boiled gently. The mixture was boiled for two and a half hours. Crusts of phosphorus separated, as noted under

the preceding preparation. Towards the end of the heating a small quantity of white crystals formed in the condenser-tube. These crystals decomposed on exposure to the air and turned yellow. They dissolved in water and alkalies, and the solutions contained phosphorus. The crystals melted when hot water was poured into the condenser-casing. They were doubtless crystals of phosphonium bromide. The reaction-product was distilled with cold water and the oil which separated was washed with soda until it had no longer an odor of phosphine; it was then extracted with ether, dried over calcium chloride, and fractioned. The crude halide boiled at 88° to 93° and, the yield was 35 grams, or 94 per cent of the theoretical quantity. The gaseous products evolved during the process were led through bromine and yielded 1.5 grams of β-butylene bromide. Other experiments gave yields of the secondary bromide ranging from 80 to 90 per cent. When the alcohol was added to the phosphorus trichloride, instead of the contrary procedure, the yield fell to 65 per cent. Less than two and a half hours' boiling resulted in low yields, as was also the case when less than one and a half times the theoretical quantity of phosphorus tribromide was used. One molecule of the alcohol heated with 1 molecule of the tribromide yielded only 39 per cent of the secondary bromide. No secondary bromide was formed when dry hydrogen bromide was led through a boiling mixture of the alcohol and zinc chloride. The hydrogen bromide for this experiment was prepared by the action of bromine upon commercial anthracene. The purified gas was led through a boiling mixture of the secondary alcohol and zinc chloride for several hours. On rectification a small amount of secondary butyl chloride was obtained but no secondary bromide.

Fractionation of the crude bromide obtained by the numerous preparations gave a heavy, colorless, fragrant liquid boiling at 91°.3 (corr.). It had the specific gravity of 1.2507 at $\frac{25°}{4°}$. Determinations of the bromine by Carius' method resulted thus:

I. 0.1530 gram substance gave 0.2090 gram AgBr.
II. 0.1773 gram substance gave 0.2419 gram AgBr.

	Calculated for C_4H_9Br.	Found. I.	II.
Br	58.39	58.12	58.05

Pure secondary butyl bromide does not react with sodium, even at the boiling-point of the halide. It gives an immediate heavy precipitate with cold alcoholic silver nitrate. Attempts to prepare secondary butyl cyanide by boiling the halide in alcoholic solution with potassium cyanide were unsuccessful.

Secondary Butyl Acetate.—Luynes[1] prepared this ester by reduction of erythrite to secondary butyl iodide, which, with silver acetate, gave the ester boiling at 111° to 113°. Lieben[2] found its specific gravity at 0° to be 0.892. We prepared the ester very readily by warming the secondary alcohol with a little more than the calculated quantity of acetyl chloride. The mixture was allowed to stand twelve hours, then poured into cold water. The light oil was washed with a solution of sodium carbonate and with water, taken up with ether, dried over calcium chloride, and fractionated. It boiled at 111°.5 to 112° (corr.) at 744 mm. pressure. The specific gravity at $\frac{25°}{4°}$ was 0.8648; at $\frac{0°}{4°}$ it was 0.8900. The ester was also formed when a mixture of sulphuric and acetic acids was added to the secondary alcohol. The yield was small, however, owing to decomposition of the alcohol by the sulphuric acid.

Secondary Butyl Propionate.—To 20 grams of the alcohol contained in a flask attached to a reflux condenser, 30 grams of propionyl chloride were slowly added. The mixture was then heated on a water-bath for one hour. The product was poured into cold water. The separated oily layer was washed with a solution of sodium carbonate, taken up with ether, dried over calcium chloride, and fractionated. The product was a fragrant liquid which boiled at 132° to 132°.5 (corr.), and had the specific gravity of 0.8657 at $\frac{25°}{4°}$. The yield of the ester (boiling-point 130° to 134°) was 28 grams, or 82 per cent of the theoretical amount. Analysis gave the following results:

[1] Jsb. d. Chem., 1868, 501.
[2] Ann. Chem. (Liebig), 180, 112.

0.3006 gram substance gave 0.7137 gram CO_2 and 0.2768 gram H_2O.

	Calculated for $C_7H_{14}O_2$.	Found.
C	64.61	64.75
H	10.77	10.23

Secondary Butyl Isovalerianate.—Five grams of the secondary alcohol were treated with 8 grams of isovaleryl chloride, as described in the previous section on the propionic ester. The isovalerianic ester boiled at 163° to 164° (corr.) at 752 mm. pressure. The yield was 8 grams, or 73 per cent of the calculated amount. The specific gravity of the ester at $\frac{20°}{4°}$ is 0.8482. Analysis gave the following results:

0.1876 gram substance gave 0.4693 gram CO_2 and 0.1893 gram H_2O.

	Calculated for $C_9H_{17}O_2$.	Found.
C	68.35	68.22
H	11.39	11.21

Disecondary Butyl Succinate.—Perkin[1] obtained the isomeric diisobutyl ester by saturating with hydrogen chloride a mixture of succinic acid and isobutyl alcohol and letting the mixture stand with occasional warming. We find the action of succinyl chloride upon the secondary alcohol to be smooth and to result in the formation of the neutral ester only, even when excess of the acyl chloride is present. Thus, 17 grams of the alcohol and 35 grams—one and two-tenths times the theoretical quantity required—of succinyl chloride were heated on a water-bath under a reflux condenser for an hour. On cooling, long silky needles crystallized out. They were washed quickly with ether and dried between filters. The crystals melted sharply at 120°; they were soluble in water and formed a strongly acid solution which gave the reaction of succinic acid. Analysis showed that the crystals were succinic anhydride. The liquid which had been decanted from the crystals was poured into cold water; the oily layer which separated was washed with a solution of sodium carbonate, taken up with ether, dried over calcium chloride, and fractionated.

[1] J. Chem. Soc. (London), **45**, 519.

The product was a fragrant liquid which boiled at 255°.5 to 256°.5 (corr.) at 750 mm. pressure. Its specific gravity at $\frac{25°}{4°}$ was 0.9735. Analysis gave the following results:

0.2117 gram substance gave 0.4884 gram CO_2 and 0.1802 gram H_2O.

	Calculated for $C_{12}H_{22}O_4$.	Found.
C	62.60	62.91
H	9.56	9.55

Secondary Butyl Benzoate.—Twenty grams of the secondary alcohol and 40 grams of benzoyl chloride were heated together for four hours under a reflux condenser on a water-bath; 1 cc. of concentrated caustic soda solution was added and the heating continued for two hours longer. After cooling, an excess of caustic soda was added and the mixture allowed to stand until it no longer smelled of benzoyl chloride. The oil which separated was washed, taken up with ether, dried over calcium chloride, and fractionated. The product was a fragrant, slightly brownish liquid which boiled at 234°.5 to 235°.5 (corr.) at 757 mm. pressure. The yield of the crude ester was 15 grams, or 66 per cent of the theoretical quantity. The specific gravity of the ester at $\frac{25°}{4°}$ was 0.9945. Analysis gave the following results:

0.2161 gram substance gave 0.5856 gram CO_2 and 0.1538 gram H_2O.

	Calculated for $C_{10}H_{12}O_2$.	Found.
C	74.15	73.90
H	7.86	7.90

Attempts to obtain the ester by the Baumann-Schotten reaction resulted unsatisfactorily; the only product was a minute quantity of a fragrant oil. Attempts to prepare the ester by the action of hydrogen chloride upon a solution of benzoic acid in the secondary alcohol were also futile. Twenty grams of benzoic acid were dissolved in 20 grams of hot secondary butyl alcohol in a flask attached to a reflux condenser, and dry hydrogen chloride was then passed through the boiling solution. In a short time the contents of the flask solidified to a crystalline mass. The solid dissolved in caustic soda and a

light, insoluble layer floated upon the alkaline liquid. The light layer was found to be secondary butyl alcohol; the solution, on acidification, gave a precipitate of benzoic acid. No ester was formed; the process thus failed on account of the slight solubility of benzoic acid in the secondary alcohol saturated with hydrogen chloride.

Disecondarybutyl (*Dimethyl-3,4-hexane*).—To 40 grams of secondary butyl bromide, diluted with 50 cc. of ether which had been dried over sodium but still contained a trace of moisture, were added 20 grams of finely shaved sodium. Reaction set in slowly, and after twenty-four hours a heavy blue deposit had formed upon the metal. The reaction was continued until further additions of sodium no longer became colored. The ethereal liquid was decanted and the residue washed repeatedly with dry ether. The combined ethereal extracts were fractionated; they contained only a small quantity of secondary butyl bromide. The blue residue was now heated; it became colorless and yielded a liquid which distilled over. The distillate boiled at 116° to 117° when rectified. It was a fragrant, mobile liquid, lighter than water, and insoluble in concentrated acids and alkalies. The yield of crude octane from 40 grams of the halide was 6 grams, or 30 per cent of the theoretical quantity. The process was repeated many times under varying conditions to discover, if possible, the cause of the low yields. When both the bromide and the ether were perfectly anhydrous, no reaction occurred even when the mixture was boiled. In one experiment the bromide dissolved in dry ether remained in contact with sodium for eight days without change. The addition of 0.5 cc. of ethyl acetate to this mixture caused a vigorous action to set in within twenty minutes, and the reaction was completed in twelve hours. The yield of crude octane in this case was 25 per cent. When no ethyl acetate was applied, the reaction required from four to five days for completion. As no gaseous products were evolved during the reaction, the cause of the low yields was sought in the residual blue substance. Until this blue compound was decomposed, no hydrocarbon was

formed. Krafft[1] has proposed that the blue substance, which is a usual product of the Wurtz-Fittig synthesis, is a sodium compound which yields the hydrocarbons on decomposition. We find the residual sodium, after the decomposition of the blue substance, still to contain much organic matter. This may account for the poor yields of the hydrocarbon. The composition and decomposition of this intermediate blue compound will be further investigated. From 200 grams of secondary butyl bromide were obtained, by many repetitions of the synthesis, 23 grams of crude disecondary butyl boiling at 110° to 117°. It was washed thoroughly with strong hydrochloric acid, caustic potash, and water, taken up with ether, dried, and fractionated. The product, although boiling nearly constantly, still contained traces of halogen, which were not removed even by repeated distillation over sodium. The halogen was finally removed by means of nascent hydrogen. The hydrocarbon was dissolved in moist ether and treated with sodium; water was added at intervals. The treatment was carried out under a reflux condenser and lasted four hours. The ethereal solution was then washed, mixed with a little concentrated hydrochloric acid, and treated with zinc; the evolution of hydrogen was kept up for twelve hours. The product was washed with caustic soda and with water, dried with calcium chloride and with sodium, and fractionated. The disecondary butyl was now completely free from halogen. Half a gram heated to 200° for two hours with fuming nitric acid and silver nitrate, in a sealed tube, gave no indication of halogen.

Disecondarybutyl is a colorless liquid of a strong odor, something like that of petroleum ether. It boils at 116° to 116°.2 (corr.) at 750 mm. pressure. Its specific gravity at $\frac{0°}{4°}$ is 0.7332; at $\frac{25°}{4°}$ it is 0.7165. Analyses resulted as follows:

I. 0.1292 gram substance gave 0.3995 gram CO_2 and 0.1801 gram H_2O.

II. 0.1281 gram substance gave 0.3953 gram CO_2 and 0.1780 gram H_2O.

[1] Ber. d. chem. Ges., **21**, 3181.

	Calculated for C_8H_{18}.	Found. I.	II.
C	84.21	84.33	84.16
H	15.79	15.50	15.44

Molecular weight determinations made by V. Meyer's method gave the following results :

	Calculated for C_8H_{18}.	Found. I.	II.
Mol. wt.	114	118.7	113.3

Attempts to prepare the hydrocarbon by the action of reduced silver upon the secondary bromide were futile ; 9 grams of the halide were boiled under a condenser for four hours with 10 grams of " molecular" silver. No silver halide was formed. The mixture was distilled off ; it all boiled at 88° to 93° and weighed nearly 9 grams. Hence it was unchanged secondary bromide upon which finely divided silver seems to have no action.

Nitration of Disecondarybutyl.—As Young and Francis[1] have shown that the isoparaffins, including diisobutyl, are readily nitrated when heated at 100° with fuming nitric acid, we studied the action of nitric acid upon disecondary butyl. Four grams of the hydrocarbon were heated with 25 grams of nitric acid, of sp. gr. 1.59, for two days on a water-bath under a reflux condenser. During the nitration much carbon dioxide was given off. The product, on dilution, yielded 0.5 gram of a fragrant, heavy, yellow oil, which gave a red color with caustic potash and was completely volatile with steam. It did not give the nitrolic acid or pseudonitrole reactions ; hence it was a tertiary nitro compound and thus differed from the nitro derivatives obtained by Worstall[2] from normal hydrocarbons. The number of nitro groups in the substance could not be determined, as the available quantity of the compound was insufficient for its purification and analysis.

Dimethyl Pinacone (Dimethyl-3,4-hexandiol-3,4).—The crude dimethyl pinacone obtained by rectification of the products of the reduction of the methylethyl ketone was fractionated repeatedly from a distillation flask, the neck of which was filled

[1] J. Chem. Soc. (London), **73**, 928.

[2] This JOURNAL, **20**, 202.

with glass beads, kept in place by a coil of platinum wire suspended from the cork. Several fractionations with this apparatus collected the greater part of the glycol in a fraction boiling at 203° to 205° (uncorr.). This, on further fractionation, yielded a product which boiled at 205° to 205°.7 (corr.) at 752 mm. pressure. Previous observers have reported the substance as boiling at 200° to 205°. The liquid, when cooled, solidified almost completely to a mass of white crystals, which melted at 49°. Zelinsky and Krapivin[1] found the melting-point to be 49°.5 when the crystals were recrystallized from ether. Recrystallization of our product from alcohol did not change the melting-point. When the crystals were not completely free from the original mother-liquor they melted at a much lower temperature. Schramm[2] has found that the crystals and liquid have the same boiling-point, and Zelinsky and Krapivin found the two to be of the same composition. Neither the crystals nor the liquid obtained by us were optically active. The two forms were identical as regards solubility in all ordinary solvents. The solubility of the substance was remarkable, as it dissolved in water and in all organic solvents; it was insoluble, however, in solutions of alkali hydroxides. No solid hydrate analogous to that formed by common pinacone could be obtained by the action of water. It seems probable that pure dimethyl pinacone is a crystalline solid which, when melted, is prevented from crystallizing by mere traces of impurities. Rohn[3] has shown that diisobutyl pinacone crystallizes with great difficulty after it has been melted. In confirmation of the view that the solid and liquid products are the same substance, is the fact that, during the fractionation of the substance, the fractions yielded crystals with greater readiness and in larger quantity as the boiling-point approached that of the pure substance. The specific gravity of the liquid dimethyl pinacone, boiling at 205° to 205°.7, was 0.9529 at $\frac{25°}{4°}$. Attempts to prepare dimethyl-3,4-dibrom-3,4-hexane by the action of dry hydrogen bromide on the dimethyl pinacone

[1] Abstract in J. Chem. Soc. (London), **64**, 390.
[2] Ber. d. chem. Ges., **16**, 1582.
[3] Ann. Chem. (Liebig), **190**, 311.

dissolved in glacial acetic acid, as proposed by Pawlow[1] for the preparation of the corresponding derivative of common pinacone, resulted unsatisfactorily. Ten grams of the glycol were dissolved in 100 grams of glacial acetic acid in a flask attached to a reflux condenser. Dry hydrogen bromide was then passed through the cooled solution for several hours. The solution turned a dark-purple color, but no crystals separated even after standing for a week. The liquid was made alkaline with caustic soda; a black oil separated and was taken up with ether, dried, and distilled at 100 mm. pressure. The oil decomposed and gave off hydrogen bromide in large quantity. Phosphorus tribromide reacts violently with the glycol; the product, after dilution, was a heavy oil. It was not further studied.

Action of Zinc and Hydrochloric Acid upon Dimethyl Pinacoline (Dimethyl-3-hexanon-4).—The action of acid reducing agents upon methylethyl ketone, as shown above, produced no secondary butyl alcohol but, nevertheless, resulted in a great loss of the ketone. If this loss were due to complete reduction of the ketone to gaseous butane the action of acid reducing agents upon dimethyl pinacoline,

$$CH_3.CH_2.C(CH_3)_2.CO.CH_2.CH_3,$$

should result in the formation of an octane. Such a result would explain the loss above mentioned. The dimethyl pinacoline was prepared as directed by Lawrinowics.[2] Five grams of dimethyl pinacone and 20 grams of 50 per cent sulphuric acid were heated together for two hours on a water-bath under a reflux condenser. The ethereal extract of the diluted product was dried and rectified. The crude dimethyl pinacoline boiling at 135° to 150° was then dissolved in ether and reduced by zinc and concentrated hydrochloric acid. The reduction extended over two days. The ethereal solution was then washed, dried over potassium carbonate, and fractionated. After removal of the ether nothing distilled over below 140°. Fraction 140°–165° weighed 2 grams; the remainder of the product boiled at 250° to 300° and weighed

[1] Ann. Chem. (Liebig), **196**, 124.
[2] *Ibid.*, **185**, 126.

nearly 2 grams. Hence no octane was formed, for normal octane boils at 125° and hexamethyl ethane at 106°. The experiment therefore sheds no light upon the loss which methyl-ethyl ketone suffers during reduction by acid reagents.

Indices of Refraction of the Secondary Butyl Derivatives.—We are indebted to Prof. G. V. Wendell, of the Institute, for the measurements of the indices of refraction of the compounds noted below. The indices were determined for the sodium ray and with respect to air at 20°. The instrument used was the improved Pulfrich refractometer:

	n_D.	Temp.
Secondary butyl alcohol	1.3949	25°.30
Secondary butyl acetate	1.3866	25°.30
Secondary butyl propionate	1.3938	25°.19
Disecondary succinate	1.4238	25°.25
Secondary butyl chloride	1.3953	25°.20
Secondary butyl bromide	1.4344	25°.25
Dimethyl pinacone	1.4521	25°.25
Disecondarybutyl	1.4038	25°.20

BOSTON, May 5, 1901.

XXXII.—ON THE ISOMORPHISM OF SELENATES AND TELLURATES.

BY JAMES F. NORRIS AND WILLIAM A. KINGMAN.

The uncertainty about the position of tellurium in the periodic system of the elements has led to a number of investigations on the isomorphism of the compounds of tellurium with those of selenium on the one hand, and with those of the platinum metals on the other. Retgers[1] found that potassium tellurate was not isomorphous with potassium selenate, but was isomorphous with potassium osmate. From a study of tellurium and its compounds, he came to the conclusion that there existed no true case of isomorphism either between selenium and tellurium, or between the compounds of these elements. The apparent isomorphism of the selenides and tellurides was, according to him, due to the fact that these compounds crystallize in the cubic system, in which substances of widely different chemical properties form mixed crystals on

[1] Ztschr. phys. Chem., 8, 70.

account of the high crystallographic symmetry of the system. Retgers, therefore, proposed to place tellurium in the eighth group in the periodic system.

In a paper published some time ago by one of us,[1] it was shown that the salts of the composition $SeBr_4.2(CH_3)_2NH.HBr$ and $TeBr_4.2(CH_3)_2NH.HBr$ are isomorphous with one another but not with the platinum salt of analogous composition. These salts do not crystallize in the cubic system. The results showed that in this case, at least, the two elements are isomorphous. On account of this fact it seemed advisable to study more fully the isomorphism of the selenates and tellurates. The potassium salts alone have been studied and were found not to form mixed crystals. These salts have the composition $K_2TeO_4.2H_2O$ and K_2SeO_4. Potassium osmate, with which potassium tellurate is isomorphous, has the composition $K_2OsO_4.2H_2O$.

It seemed to us that the failure to form mixed crystals of potassium selenate and potassium tellurate might be due to the fact that one salt contained water of crystallization, while the other was anhydrous. We, accordingly, attempted to find two salts of selenic and telluric acids which either were anhydrous or contained the same number of molecules of water of crystallization. In this we were unsuccessful, but the results which have been obtained are of sufficient interest to warrant publication.

The ammonium and lithium salts of the two acids are described as anhydrous in the literature. The tellurates of these bases we found to be uncrystallizable gums, which, therefore, could not be used in the investigation. As no selenate has been described which has the same number of molecules of water as the analogous tellurate, we undertook the preparation of some new salts of these acids.

Cerium tellurate was first made. It seemed advisable to make this compound since cerium selenate crystallizes with three different quantities of water. Cerium carbonate was insoluble in telluric acid. When a solution of sodium tellurate was added to a solution of cerium sulphate, a white pre-

[1] This JOURNAL, **23**, 486.

cipitate was formed, which was shown to be cerium tellurate.

As the cerium salts could not be used to study the isomorphism of the selenates and tellurates the rubidium and caesium salts were prepared. The neutral selenates of these metals have been made and carefully studied by Tutton.[1] The salts are anhydrous and isomorphous with the corresponding sulphates. Caesium tellurate was prepared and found to be a well crystallized compound. As the salt contained 3 molecules of water, the acid salts were next made, as the chances for the formation of anhydrous salts in this case were greater. There was also a difference in composition in these salts. The acid selenates of rubidium and caesium are very soluble, well-crystallized, anhydrous salts; the acid tellurates, on the other hand, are much less soluble, crystallize with difficulty, and contain 0.5 molecule of water of crystallization. Notwithstanding this difference, the isomorphism of the salts was investigated with the result that mixed crystals of the compounds could not be formed.

The question of the isomorphism of selenium and tellurium cannot be settled, it appears, by a study of salts of selenic and telluric acids. All of the tellurates except those of the alkali metals are insoluble, and the soluble salts do not resemble the analogous selenates in crystal form, solubility, or content of water of crystallization.

EXPERIMENTAL.

Rubidium Hydrogen Tellurate, $RbHTeO_4.\frac{1}{2}H_2O$.—This salt was made by mixing solutions of rubidium carbonate and telluric acid containing the theoretical quantities of the two substances for the acid salt: 1 gram of crystallized telluric acid and 0.5 gram rubidium carbonate were used. When the solution was concentrated by heat, an amorphous powder separated. On spontaneous evaporation a crystalline crust appeared. These two forms were analyzed for water and telluric acid.

In determining telluric acid, a solution of about 0.5 gram of salt in 50 cc. hydrochloric acid (sp. gr. 1.12) was boiled until the volume was reduced about two-thirds. The chlorine

[1] J. Chem. Soc., 71, 846.

which was evolved was drawn, by means of a current of air, through a strong solution of potassium iodide, which was kept cold by ice-water. The liberated iodine was titrated with a solution of sodium thiosulphate. One atom of tellurium in the form of telluric acid liberates 2 atoms of chlorine. The determinations of tellurium were all made with the anhydrous salts which were dried to constant weight at 120°.

The results of the analyses follow: Analysis I is of the amorphous powder and Analysis II is of the crystalline crust:

	Calculated for $RbHTeO_4.\frac{1}{2}H_2O$.	Calculated for $RbHTeO_4$.	Found. I.	Found. II.
H_2O	3.16	....	3.73	3.49
Te	....	44.44	44.82	44.91

The salt is soluble in about 20 parts of cold water, but slightly more soluble in hot water.

Caesium Hydrogen Tellurate, $CsHTeO_4.\frac{1}{2}H_2O$.—On evaporation of a solution containing 1 gram of caesium carbonate and 1.5 grams crystallized telluric acid and subsequent cooling, a white amorphous powder separated. Later a crystalline crust was formed, which appeared to consist of very small cubical crystals. The salt was less soluble than the corresponding rubidium salt. It required about 30 parts of water for its solution.

An analysis of the crystals resulted as follows:

	Calculated for $CsHTeO_4.\frac{1}{2}H_2O$.	Calculated for $CsHTeO_4$.	Found.
H_2O	3.96	....	4.19
Te	....	39.17	39.50

Rubidium Hydrogen Selenate, $RbHSeO_4$.—This salt was prepared by adding to a solution of rubidium carbonate twice the quantity of selenic acid required to neutralize it. The solution, on evaporation, yielded well-formed crystals which were soluble in about their own weight of water. The salt was very hygroscopic. It was shown to be anhydrous by heating to 120° a weighed quantity of the salt which had been dried over sulphuric acid. The selenium was determined in the following way: About 0.4 gram salt was dissolved in 25 cc. concentrated hydrochloric acid diluted to 100 cc. The solution was

boiled for one hour, care being taken to keep the volume between 75 and 100 cc. The selenium in the resulting solution was precipitated by sodium hydrogen sulphite, dried, and weighed. The analysis resulted as follows:

	Calculated for $RbHSeO_4$.	Found.
Se	33.12	33.32

Caesium Hydrogen Selenate, $CsHSeO_4$.—This salt was prepared from caesium carbonate and selenic acid. The solution was evaporated nearly to dryness before crystals appeared. The salt crystallizes in large flat plates with pointed ends and is exceedingly hygroscopic. The compound was shown to have no water of crystallization. A selenium determination gave 28.63 per cent instead of 28.80 per cent, the theoretical amount.

Rubidium Tellurate, $Rb_2TeO_4.3H_2O$.—As rubidium tellurate is decomposed by carbon dioxide, the salt cannot be made from rubidium carbonate and telluric acid. It was prepared by neutralizing the acid with rubidium hydroxide. An excess of about 25 per cent of the base was added, and the solution was evaporated in a vacuum desiccator over sulphuric acid. The salt crystallizes in prisms terminated by pyramids, and is soluble in about 10 parts of water. The analysis resulted as follows:

	Calculated for $Rb_2TeO_4.3H_2O$.	Found.
H_2O	12.96	13.10
Te	35.29	34.74

Attempt to Form Mixed Crystals of the Acid Rubidium Salts of Selenic and Telluric Acids.—On account of the fact that there was but 0.5 molecule of water in rubidium hydrogen tellurate, we studied the isomorphism of this salt with rubidium hydrogen selenate. In working out an analytical method for the determination of a selenate in the presence of a tellurate, we studied a method of separation of selenium and tellurium. This method did not give results sufficiently accurate for it to be recommended for quantitative work, but it served to test the isomorphism of the compounds under investigation.

When telluric and selenic acids are boiled with strong hydrochloric acid, they are reduced to the lower state of oxidation. If to such a solution a strong solution of potassium iodide is added, the selenium is precipitated and the tellurium is converted into tellurium iodide, which remains in solution in the excess of potassium iodide. These reactions were tested quantitatively. 0.2436 gram rubidium hydrogen selenate was boiled for an hour with 25 cc. concentrated hydrochloric acid diluted to 100 cc., care being taken to keep the volume between 75 and 100 cc. After cooling, a saturated solution of potassium iodide was added in large excess. The precipitated selenium was washed by decantation with warm potassium iodide solution, then with water, and finally, after drying at 110°, was weighed. 0.0849 gram of selenium was obtained. This corresponds to 34.85 per cent instead of 34.42 per cent, the amount required by theory. This experiment showed that selenium could be determined in this way with a fair degree of accuracy.

The separation of selenium from tellurium was studied by treating a solution of selenium dioxide and tellurium dioxide in hydrochloric acid with potassium iodide, filtering, washing with potassium iodide, and weighing the selenium. In two experiments about 0.35 gram of tellurium dioxide was mixed with weighed quantities of selenium dioxide.

Gram SeO_2 used.	Gram Se used.	Gram Se found.
0.1521	0.1082	0.1101
0.2041	0.1452	0.1527

Although these results are far from accurate the method is so rapid and convenient that it was used. The results obtained were found sufficiently accurate for the purpose.

An aqueous solution of molecular quantities of the acid rubidium salts of selenic and telluric acids was allowed to evaporate spontaneously. The first two crops of crystals were analyzed in the manner described above. The selenium determinations gave the following results:

I. 0.3029 gram of first crop of crystals gave 0.0029 gram Se.

II. 0.3327 gram of second crop of crystals gave 0.0087 gram Se.

	Calculated for $RbHTeO_4.RbHSeO_4$.	Found. I.	II.
Se	13.59	0.95	2.61

These results show that the two salts are not isomorphous.

BOSTON, May 6, 1901.

Contributions from the Kent Chemical Laboratory of the University of Chicago.

ON GOLD HALIDES.

BY FELIX LENGFELD.

Though the gold halides have been extensively investigated by Thomsen,[1] Schottländer,[2] Krüss,[3] and others, the data given are frequently contradictory, and it therefore seemed that some results obtained in the course of an attempt to obtain silver salts of halauric acids might be of interest.

Aurous Chloride.

Aurous chloride is easily made by heating auric chloride to 175° for several days.[4] The decomposition of the auric salt is complete and the product is almost pure aurous chloride. For instance, one specimen contained 85.95 per cent gold and 14.06 per cent chlorine (calculated 84.76 per cent and 15.24 per cent). Below 175° auric salt is left, above 175° aurous chloride decomposes more easily. Aurous chloride is insoluble in water and dilute nitric acid. Concentrated nitric acid gradually decomposes it, auric salt going into solution leaving a residue of gold. On adding nitric acid to its ammoniacal solution a white curdy precipitate resembling silver chloride is formed. This could not be analyzed, as it decomposes when washed, forming auric salt and free gold. Aurous chloride dissolves in hydrochloric and hydrobromic acids and in the alkali chlorides and bromides with decomposition. With bromides the decomposition is more rapid than with chlorides. With a solution of potassium bromide it gives gold and a brownish-red liquid that contains no free bromine but potassium chloraurate and bromaurate,

$$4KBr + 12AuCl = KAuBr_4 + 3KAuCl_4 + 8Au.$$

[1] J. prakt. Chem., (2), **13**, 337; Therm. Unters., **3**, 390, etc.

[2] Ann. Chem. (Liebig), **217**, 312.

[3] Ber. d. chem. Ges., **20**, 211, 2634; Ann. Chem. (Liebig), **238**, 241; etc.

[4] Pignier: J. Pharm., **6**, 84; **8**, 157. Thomsen: *Loc. cit.* Krüss: Ann. Chem. (Liebig), **237**, 276.

A solution of sodium chloride takes it up with little decomposition and is at first almost colorless. A double salt, perhaps $NaAuCl_3$, is formed. The double salt is unstable for, on standing, gold is deposited (often as an excellent mirror) the solution becomes yellow and contains the salt $NaAuCl_4$.

Aurous chloride is slowly decomposed by ether, alcohol, and acetone, auric chloride going into solution.

Aurous Bromide.

Aurous bromide may be obtained almost pure by heating bromauric acid on the water-bath three hours and then to 105° for twelve hours.[1] No auric salt is left, but usually a little gold is set free. Analysis showed 72.68 per cent gold and 27.09 per cent bromine (calculated 71.14 and 28.86 per cent). The substance is gray, amorphous, and resembles the chloride. It is insoluble in water, nitric or sulphuric acid, is slowly decomposed by alcohol, ether, acetone, and moist chloroform, and dissolves with partial decomposition in ammonia. Nitric acid, added to its ammoniacal solution, gives an unstable precipitate partly soluble in ammonia, so that after several repetitions of the operation all the salt is decomposed. Potassium cyanide dissolves the salt without decomposition. Potassium bromide gives potassium bromaurate and gold. Chlorides act like bromides, but more slowly. Hydrobromic acid gives bromauric acid and gold, and hydrochloric acid acts in a similar manner.

Auroso-auric Bromide (*Aurous Bromaurate*).

The existence of this salt and of the corresponding chloride has been affirmed by Thomsen[2] and denied by Krüss and Schmidt.[3] Peterson[4] established beyond a doubt the existence of the chloride, but was not so successful with the bromide. Finely divided gold precipitated by ferrous sulphate was dried at 105° and kept *in vacuo* over phosphoric anhydride for two weeks. An amount weighing 6.1286 grams was treated with excess of bromine in a closed crucible, the bro-

[1] See Thomsen: *Loc. cit.*

[2] *Loc. cit.* and J. prakt. Chem., (2), **37**, 105.

[3] Ber. d. chem. Ges., **20**, 2640; J. prakt. Chem., (2), **38**, 82.

[4] J. prakt. Chem., (2), **46**, 328; **48**, 88.

mine evaporated in a current of dry air, and the crucible then kept *in vacuo* over phosphoric anhydride to constant weight. The mass was finely powdered and again brought to constant weight. This was repeated a number of times. There was of course a slight loss in the powdering and transferring. This has been taken into account, and to avoid complication all the figures have been referred to the quantity of gold originally taken. In the first operation the gold took up 4.7440 grams bromine, in the next 0.2749, then 0.1373, 0.0987, 0.0541, 0.1059, 0.1060, altogether, 5.5209 grams. Thus the first time the gold took up 77.24 per cent of its weight of bromine, and in all 90.08 per cent. To form the compound Au_2Br_4 it must take up 81.07 per cent bromine, and to form auric bromide, $AuBr_3$, 121.6 per cent. This would seem to indicate the existence of the compound Au_2Br_4, especially as a number of experiments showed that finely powdered gold always takes up about 80 per cent of its weight of bromine at the first treatment, and then adds bromine very slowly. If the operation is repeated often enough gold will probably take up 120 per cent of bromine, or even more, as a little is added each time. This action, however, seems due to the presence of moisture. Water readily acts on the compound Au_2Br_4, setting free gold, and this adds bromine. The longer the powder is exposed to the air the more bromine is taken up.

It may be urged that auric bromide is first formed and protects the gold from further attack by forming a coating. This seems disproved by the action of ether, in which the tribromide is easily soluble. The auroso-auric bromide seems only slowly affected by anhydrous ether at zero, and this suggested a method of purification. A product prepared by treating gold with bromine seven times and containing 47.3 per cent bromine was treated with ice-cold ether until the liquid, which at first was highly colored, was perfectly colorless. The residue was then dried and analyzed. It contained 61.41 per cent gold and 38.14 per cent bromine (calculated for Au_2Br_4 55.22 per cent gold and 44.78 per cent bromine; for AuBr 71.12 per cent gold; and for $AuBr_3$ 45.08 per cent). It would thus seem to be a mixture of gold or aurous bromide

and auric bromide, or of gold or aurous bromide and aurosoauric bromide. The action of water shows that it is not a mixture of auric bromide and gold or aurous bromide in which grains of the auric salt are protected from the solvent action of the ether by a coating of aurous bromide or gold. Aurous bromide and gold are insoluble in water, and would therefore protect from that liquid as well as from ether. True, aurous bromide is decomposed by water but slowly. The substance washed with ether is a mixture of aurous bromaurate, Au_2Br_4, with aurous bromide or gold, probably the latter, for the ethereal solution of auric bromide if not free from traces of moisture reacts with aurous bromide to form bromauric acid and gold. Analysis of the ether solution always showed besides organic oxidation-products more than 3 atoms of bromine to 1 of gold.

The action of bromine upon gold is, therefore, attended with the formation of a steel-blue aurous bromaurate, stable in the absence of water, easily decomposed at ordinary temperatures by water and many organic solvents.

Auric Chloride and Auric Bromide.

These salts are too well known to require much discussion. They easily go into the corresponding halauric acids and gold oxide or gold, the bromide so readily that it is difficult to obtain it pure. If aurous bromaurate is treated with ether and the solution evaporated in a current of air, as recommended by Thomsen,[1] much bromauric acid is obtained unless the ether be pure and dry, and the temperature low. If aurous bromaurate is treated with little ice-cold water and the solution kept cold in a vacuum desiccator over phosphoric anhydride until the water has evaporated, pure gold tribromide is left. Analysis showed 45.35 per cent gold and 54.85 per cent bromine (calculated, 45.08 per cent and 54.92 per cent.) If the temperature is not kept low, there is formation of bromauric acid. Some of the substance which formed from a solution kept at the ordinary temperature contained 3.16 per cent free gold and 2.8 per cent water, corresponding to about 30 per cent of the compound $HAuBr_4.3H_2O$.

[1] *Loc. cit.*

Chlorauric Acid.

There has been some discussion regarding the existence of the compound $HAuCl_4.4H_2O$.[1] There is no doubt that a compound of the composition $HAuCl_4.3H_2O$ is obtained when the salt is kept in a moderately dry atmosphere, *i.e.*, over sulphuric acid, calcium chloride, or potassium hydroxide. Analysis showed 35.73 per cent to 36 per cent chlorine, and 49.90 per cent to 50.24 per cent gold (calculated 35.98 per cent and 50.04 per cent). Kept for two weeks *in vacuo* over phosphoric anhydride the salt contained 51.86 per cent gold (calculated for $HAuCl_4.2H_2O$, 52.39 per cent). However, the substance was not homogeneous and a considerable portion was insoluble, showing that the loss of water of crystallization was accompanied by decomposition, and making the existence of a compound of the formula $HAuCl_4.2H_2O$ appear improbable. Thomsen bases his belief in the existence of the salt $HAuCl_4.4H_2O$ mainly on thermochemical data. When the compound $HAuCl_4.3H_2O$ is left in the air it rapidly deliquesces. Attempts to identify a definite compound failed. The pasty mass first obtained was spread on clay plates, and the dry substance analyzed. One analysis gave 47.71 per cent gold (calculated for $HAuCl_4.4H_2O$, 47.86 per cent), but another gave 46.32 per cent, and others even lower. Hence if the compound $HAuCl_4.4H_2O$ exists, it readily takes up more water in a moist, and loses water in a dry, atmosphere. The compound $HAuCl_4.3H_2O$, on the other hand, is stable and loses water only with decomposition.

Bromauric Acid.

This substance was obtained by Thomsen's method,[2] which I afterwards modified slightly. The finely powdered and dry gold was left in a covered crucible with an excess of bromine over night, the cover removed, and the bromine evaporated at the room temperature. The mass was then powdered and kept over night in a closed vessel with the requisite quantity of hydrobromic acid and a slight excess of bromine. On ex-

[1] Schottländer: Ann. Chem. (Liebig), 217, 312; Thomsen: Ber. d. chem. Ges., 16, 1585.

[2] *Loc. cit.*

posing to the air, bromauric acid separated. It was powdered and spread on glazed tiles to dry. The air-dried bromauric acid contained 6 molecules of water, though Thomsen gives it the formula $HAuBr_4.5H_2O$. Kept over drying agents it lost 3 molecules water, but again took them up on exposure to the air. Analyses of six samples, treated in different ways, gave 31.16 to 31.47 per cent gold, and 50.81 to 50.91 per cent bromine (calculated for $HAuBr_4.6H_2O$, 31.47 per cent and 51.12 per cent; for $HAuBr_4.5H_2O$, 32.40 per cent and 52.63 per cent). In one lot the hydrogen was determined by combustion.

0.5142 gram salt gave 0.0958 gram H_2O.

	Calculated for $HAuBr_4.6H_2O$.	Calculated for $HAuBr_4.5H_2O$.	Found.
H	2.076	1.757	2.07

Kept over potassium hydroxide, calcium chloride, sulphuric acid, or phosphorus pentoxide, the salt loses 3 molecules of water, but can lose no more without decomposition. Left in a desiccator with potassium hydroxide over night, one sample gave 32.49 per cent gold, another 32.56 per cent gold, corresponding to $HAuBr_4.5H_2O$ (calculated, 32.4 per cent gold), but they lost water on standing longer in the desiccator and took up water on exposure to air. On standing a few days with a drying agent the weight becomes constant, and there is no further loss after a week *in vacuo* over phosphoric anhydride.

Analyses showed from 34.40 to 34.68 per cent gold and 54.35 to 54.75 per cent bromine (calculated for $HAuBr_4.3H_2O$, 34.70 and 54.87 per cent). The energy with which the last molecules of water are held is illustrated by the behavior of the ether solution. The compound $HAuBr_4.6H_2O$ dissolves in chloroform or ether and may be obtained unchanged on evaporation of the solvent. If the ether solution is dried with calcium bromide there is a considerable precipitation of a gold salt, perhaps a double bromide of gold and calcium, and the solution becomes of a much lighter color. If the ether is now evaporated in a current of dry air the compound $HAuBr_4.3H_2O$ is left. Analysis showed 34.16 per cent gold and 54.37

per cent bromine. As the balance might be ether, a combustion was made.

0.6268 gram substance gave 0.0099 gram CO_2 and 0.0734 gram H_2O.

	Calculated for $HAuBr_4.3H_2O$.	Found.
C	....	0.43
H	1.22	1.30

The carbon indicates the presence of a little organic purity.

Silver Salts of Halauric Acids.

Though Schottländer[1] found that silver carbonate gives with chlorauric acid a mixture of silver chloride and auric oxide,

$$2HAuCl_4 + 4Ag_2CO_3 = 8AgCl + Au_2O_3 + H_2O + 4CO_2,$$

Jörgensen's[2] work with silver chlorplatinate makes the existence of silver halaurates probable. If to a solution of chlorauric acid or a chloraurate a silver salt is added in the proportion of 1 equivalent silver to 4 equivalents chlorine, several reactions seem possible. Silver chloraurate may be formed and precipitated as such or it may be decomposed into silver chloride and gold trichloride. Silver chloride may be formed as a primary product so as to leave three-fourths of the chloraurate unchanged, or so as to convert all of it into gold tribromide. The reactions may be represented as follows:

$$HAuCl_4 + AgX = AgAuCl_4 + HX;$$
$$4HAuCl_4 + 4AgX = 4AgCl + AuX_3 + HX + 3HAuCl_4;$$
$$HAuCl_4 + AgX = AuCl_3 + AgCl + HX.$$

Chlorauric acid was dissolved in ice-cold water and a cold solution of silver nitrate (1 mol. to 1 mol.) added. A yellow precipitate was formed at once, but almost immediately it became darker. It was washed and analyzed. In the solution the proportion of gold to chlorine was 1 atom gold to 3.5 atoms chlorine. This and the analysis of the precipitate showed that at least two, and probably all three, of the reactions indicated occur. No simple reaction apparently took

[1] Ann. Chem. (Liebig), 217, 312.
[2] Ztschr. anorg. Chem., 22, 446.

place when sodium chloraute or chlorauric acid was treated with silver carbonate or silver nitrate in absolute alcohol. The interpretation of the results was complicated, as the reactions took some time, owing to the insolubility of the silver carbonate, and alcoholic solutions of auric chloride soon deposit gold and retain chlorauric acid, so that the solution showed 4 atoms chlorine to 1 atom of gold. Analysis of the precipitates left no doubt, however.

As sodium chloraurate decomposes before losing its water of crystallization, anhydrous potassium chloraurate was dissolved in absolute alcohol and shaken with silver carbonate. The precipitate contained but little gold, and the solution analyzed at once gave almost exactly 3 (3.07) atoms chlorine to 1 of gold. On standing, the solution deposited gold, and after two days contained 4 atoms chlorine to 1 of gold, thus acting exactly like an alcoholic solution of auric chloride. The reaction, therefore, is:

$$2KAuCl_4 + Ag_2CO_3 = K_2CO_3 + 2AgCl + 2AuCl_3.$$

This seems to be the main reaction even if water is used instead of alcohol.

The action of silver nitrate on an alcoholic solution of potassium chloraurate seems more complicated, as the solution contains 3.4 atoms of chlorine to 1 of gold. Potassium chloraurate and silver salts were shaken together in anhydrous ether but there was no action. Potassium chloraurate is insoluble in anhydrous but not in ordinary ether. In the presence of a little water or alcohol it is more soluble in ether than the sodium salt, though the latter is not insoluble in absolute ether. The remarkable difference in the behavior of sodium and potassium chloraurates toward silver salts may throw some light on the rôle of the water of crystallization in the former. The latter, in solution, acts towards silver salts like a mixture of potassium and gold chlorides. Bromauric acid, in aqueous and alcoholic solutions, acts toward silver salts in about the same way as chlorauric acid, though the reaction is further complicated by the greater instability of some of the products.

The work will be continued, especially in the direction of organic gold compounds.

The analyses were usually carried out by treating the gold compound in water or water and acetic acid with magnesium ribbon. The excess of magnesium was dissolved in acetic acid and the gold washed with nitric acid and water. In the filtrate the halogen was determined as usual. If only the gold content was required this could, in the absence of other non-volatile ingredients, be determined by heating in a crucible, care being taken first to bring the cover to redness so as to decompose any volatile gold compound. The gold salt may also be decomposed by formic aldehyde in alkaline solution. This method gives good results for gold, but cannot be depended upon for halogen.

Contributions from the Sheffield Laboratory of Yale University.

LXXXV.—ON THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.

III. THE SOLUBILITY OF ALUMS AS A FUNCTION OF TWO VARIABLES.

By James Locke.

In my second paper in this series[1] I attempted to show that a definite gradation can be traced in the solubility of the alums of aluminium, vanadium, chromium, and iron, severally, with ammonium, thallium, rubidium, and caesium. When the solubilities at 25° of the sixteen compounds considered, expressed in gram-molecules per liter of water, are plotted as a function of the atomic weights of the trivalent metals, a figure of remarkable regularity is obtained. The solubilities of the alums of aluminium, vanadium, and iron, with any given alkali metal, increase with the atomic weights of the trivalent metals; and this increase becomes the more pronounced as we pass from the caesium alums through those of rubidium and thallium, to the ammonium salts, successively. But the alums of chromium, a metal which stands between vanadium and iron in its atomic weight, are much less soluble than those of

[1] This Journal, **26**, 166.

either of the latter metals. The sharp break in the curves, caused by this behavior of the chromium salts, indicates that although the method of plotting employed illustrates the general gradation of the solubilities, the latter cannot truly be regarded as a function of the atomic weights. The solubilities, as determined, are as follows:

$M^{III} =$	Al.	V.	Cr.	Fe.
$M^{I} =$ Cs	0.013	0.0204	0.0151	0.045
Rb	0.059	0.177	0.078	0.293
Tl	0.177	0.573	0.212	0.799
NH_4	0.387	1.210	0.407	1.659

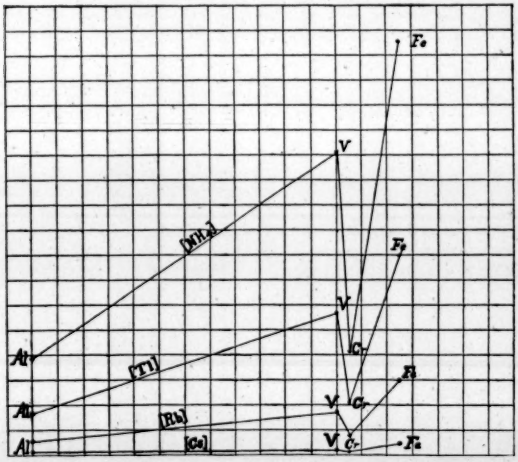


Fig. 1.

Fig. I reproduces these relations. For the sake of clearness, the values are slightly increased along the x-axis. The lines joining the vanadium and chromium alums of each univalent metal should, in reality, be nearly perpendicular to the x-axis.

A careful examination of this figure gives, at the outset, one

striking result which, if it is also to be observed in solubility charts of other series of homologous compounds, may lead to a great advance in our knowledge of the relative influence of analogous elements upon their compounds. *The lines joining the solubility points of the successive univalent metals with two given trivalent metals, have approximately a common point of intersection.* Thus, the line joining the solubility-points of the caesium alums of vanadium and aluminium, on prolongation, meets that of the thallium alums of the same metals, in the point, $x = 16.25$, $y = 0.11$;[1] the points of intersection of the remaining corresponding lines, vary only slightly from this, and on either side of it. The intersection-points of all the aluminium-vanadium lines with one another follow:

	Cs–Rb.	Rb–Tl.	Cs–Tl.	NH_4–Cs.	NH_4–Rb.	NH_4–Tl.
$x =$	18.1	16.3	16.25	16.0	15.7	15.1
$y =$	1.1	0.11	0.11	1.17	0.15	0.12

The following are the points of intersection of the vanadium-chromium lines:

	Rb–Cs.	Tl–Cs.	Tl–Rb.	NH_4–Cs.	NH_4–Rb.	NH_4–Tl.
$x =$	52.99	52.6	52.65	52.6	52.6	52.53
$y =$	1.2	1.3	0.8	1.4	1.45	5.3

In both of these series the nearest approximation of the points of intersection to a single point is seen to be in the case of those lines which intersect at the greatest angle. The most marked deviation is that of the (AlCs–VCs) and (AlRb–VRb) lines in the first series, and that of the (VTl–CrTl) and (VNH_4–$CrNH_4$) lines in the second; that is, where the lines in question are most nearly parallel, and where, therefore, unavoidable error of experiment would produce the greatest divergence. The various other lines, such as those of (FeM^I–CrM^I), (FeM^I–AlM^I), or (CrM^I–AlM^I), show a similar relation as regards their points of intersection, and it must be assumed, therefore, that *the points representing the solubilities stand in fixed mathematical relation to one another.*

This being so, the derivation of a general formula for the calculation of the solubility of the sixteen alums in question is a comparatively simple matter. The first step involved is the

[1] The unit on the *x*-axis being the atomic unit, while that on the *y*-axis is one-hundredth of a gram-molecule.

empirical determination of the fixed points, of which the observed points of intersection are approximations. Of these, the three giving respectively the intersections of the lines (VM^{I}–AlM^{I}), (VM^{I}–CrM^{I}), and (CrM^{I}–FeM^{I}) are required.

The points finally selected, as most nearly satisfying all the points of intersection, are as follows:

$$\text{For } (VM^{I}\text{–}AlM^{I}) \begin{cases} x = 16.1 \\ y = 0.8 \end{cases}$$

$$\text{For } (VM^{I}\text{–}CrM^{I}) \begin{cases} x = 52.61 \\ y = 1.5 \end{cases}$$

$$\text{For } (CrM^{I}\text{–}FeM^{I}) \begin{cases} x = 50.81 \\ y = 0.6 \end{cases}$$

Radii drawn from these points gave, by intersection with perpendiculars raised on the y-axis at points corresponding to the atomic weights of the trivalent metals, the following solubilities in gram-molecules. Under D is given the variation from the observed solubilities:

m^{III} = Al.	D.	V.	D.	Cr.	D.	Fe.	D.
m^{I} = Cs 0.012	−0.001	0.0209	+0.0005	0.0169	+0.0018	0.0498	+0.0048
Rb 0.064	+0.005	0.1878	0.0108	0.0734	−0.0046	−0.2776	−0.0164
Tl 0.182	+0.005	0.5670	−0.006	0.2014	−0.0106	0.7922	−0.0068
NH_4 0.382	−0.005	1.209	−0.001	0.4182	−0.0112	1.6643	+0.0016
Average error	+0.001		−0.001		−0.0005		−0.0043

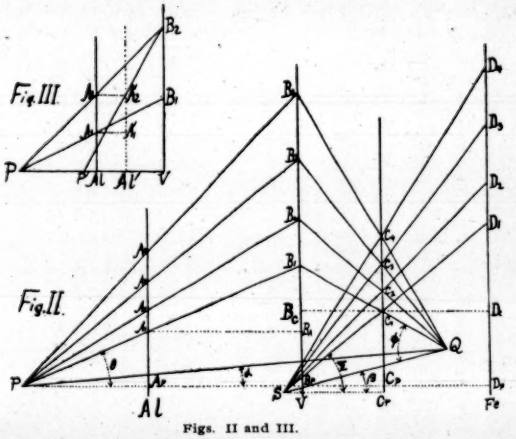
As is seen, the agreement between the observed and calculated solubilities is in the main very satisfactory. In more than half the cases, the difference does not exceed 0.005 gram-molecules. The average molecular weight of an alum is about 300, and the error represented by a difference of 0.001 gram-molecule therefore means about 0.3 gram per liter. As the majority of my determinations were made with quantities of solutions containing about 3 grams of water, an error of this magnitude would therefore represent, on the average, less than a milligram in weight; or in the case of the ammonium alums, where the dissolved salts were determined as sesquioxides, less than 0.5 milligram. A very slight variation in temperature, in the case of the more soluble alums, introduces a still greater error. At 30°, 1 liter of water dissolves 0.467 gram-molecule ammonium aluminium alum, and 0.495 gram-molecule ammonium chromium alum. The increase in solu-

bility for 5° is, therefore, in the one case 0.080, and in the other 0.088 gram-molecule. Assuming that for so short an interval the solubility is directly proportional to the temperature, a variation of ±0°.2 would cause an error of more than 0.003 gram-molecule. The range of solubility of the alums is so great that errors of such magnitudes would have little influence upon the determination of the general solubility relations of the salts; and such relations were all that I had hoped to establish by the work embodied in my last paper. If we take into account the effect which the more or less extensive hydrolytic dissociation of the sulphates of the trivalent metals would have upon the solubility of the alums,[1] the variation between the solubilities, calculated and observed, is in almost every case well within the limit of permissible error. In the derivation of the constants used in this paper, therefore, the calculated results will be taken as correct.

The prolongation of the aluminium-vanadium lines and of the vanadium-chromium lines to their respective points of intersection, yields a series of triangles which have a common base in the line connecting these points. A similar set of triangles is given by the intersection of the vanadium-chromium lines with those of chromium-iron. The resulting figure, somewhat distorted in its proportions, is shown in Fig. II.

The perpendiculars, *A*Al, *B*V, *C*Cr, and *D*Fe, and the fixed points, *P*, *Q*, and *S*, being given, the points of intersection of the radii from *P*, *Q*, and *S* with the perpendiculars *B*V, *C*Cr, and *D*Fe are necessarily determined by the position of the points of intersection of the corresponding radii from *P* with the perpendicular *A*Al. Now the points A_1, B_1, C_1, and D_1, represent the solubilities of the caesium alums of the successive trivalent metals; A_2, B_2, C_2, and D_2 those of the rubidium alums, etc. The line A_1P makes a definite angle, θ, with the x-axis, and the points B_1, C_1, D_1, are accordingly determined by the value of this angle. If we substitute rubidium for caesium, θ receives another value, and B, C, and D become B_2, C_2, D_2. The effect of the substitution of any one alkali metal for

[1] This, of course, also applies to the formation of small quantities of basic salts on evaporation of the solutions for analysis.



Figs. II and III.

another in the alums of a trivalent metal is, therefore, always measurable, directly or indirectly, by the difference in the values of θ peculiar to the alkali metals in question.

The absolute values of the angle θ are fixed by the relative positions of the perpendiculars AAl and BV upon the x-axis; but these do not affect its relative values; for if AAl, for instance, be moved in either direction, the point P still retains its y-value, and therefore the relation

$$\frac{\tan\theta_1}{\tan\theta} = \frac{A_P A_2}{A_P A_1} = \frac{A_P A_2'}{A_P A_1'} = \text{constant.}$$

remains the same in all cases. θ is accordingly a variable peculiar to the alkali metals in the compounds, and independent of the trivalent metals. The same is true of the variable distance $PA(=\rho)$, which depends directly upon the value of θ, in the sense

$$\rho \sin\theta = AA_P = \text{const.},$$

for each of the alkali metals, and without regard to the position of the perpendiculars.

The effect of the trivalent metals upon the solubility is also given by a variable which has a constant value for each. As intercepts of two sides of a triangle by parallel lines, the relations obtain :

$$\frac{A_1B_1}{A_1P} = \frac{A_2B_2}{A_2P} = \frac{A_3B_3}{A_3P} = \ldots\ldots\ldots = k;$$

$$\frac{B_1C_1}{C_1Q} = \frac{B_2C_2}{C_2Q} = \ldots\ldots\ldots\ldots\ldots = k_1;$$

$$\frac{C_1D_1}{SC_1} = \frac{C_2D_2}{SC_2} = \ldots\ldots\ldots\ldots\ldots = k_2.$$

These constants, k, k_1, and k_2, are independent of the value of the angle θ, and, therefore, of the univalent metals in the alums. They are also independent of the positions of the perpendiculars AAl, etc. If the relative positions of AAl and BV be altered, for instance, until P becomes P' (Fig. III), the ratio between the new intercepts, $\frac{A_1'B_1'}{A_1'P'}$, is still the same as $\frac{A_1B_1}{A_1P}$, or k.

We have, furthermore, the relation

$$\frac{B_1B_2}{A_1A_2} = \frac{B_2B_3}{A_2A_3} = \ldots\ldots \frac{PB}{PA} = \frac{\rho(k+1)}{\rho} = k+1.$$

Similarly, for the vanadium and chromium alums,

$$\frac{C_1C_2}{B_1B_2} = \frac{C_2C_3}{B_2B_3} = \ldots\ldots = \frac{C_1Q}{C_1Q + K_1C_1Q} = \frac{1}{k_1+1},$$

and for those of chromium and iron,

$$\frac{D_1D_2}{C_1C_2} = \frac{D_2D_3}{C_2C_3} = \ldots\ldots = \frac{SC_2 + K_2SC_2}{SC_2} = k_2+1.$$

Now A_1A_2 represents the difference in solubility of the aluminium alums of rubidium and caesium ; C_1C_2, that of the chromium alums, etc. If we call the difference in the solubility of the alums of a given trivalent metal with two alkali metals the "increment of solubility for the latter (*e. g.*, Incr. $Al_{Rb\text{-}Cs}$), we arrive at the general law :"

The ratio between the increments of solubility of the corresponding alums of two trivalent metals for any two alkali metals is constant.

The constant k indirectly represents, therefore, the effect of the substitution of vanadium for aluminium in the alum of a given univalent metal; k_1 that of chromium for vanadium, etc. And since the value of these constants is not affected by the relative positions of the perpendiculars upon the x-axis, the atomic weights of the trivalent metals have no determining influence upon them. The solubilities cannot, therefore, be regarded as a function of these atomic weights.

The values of the constants k, etc., for the calculated solubilities are as follows:

$$k = 2.2110$$
$$k_1 = 1.9608$$
$$k_2 = 3.0213$$

By substitution we have, furthermore, for the ratio between the solubility-increments of the alums of other pairs of trivalent metals,

$$\frac{C_1C_2}{A_1A_2} = \frac{\text{Incr. } Cr_{m^2-m^1}}{\text{Incr. } Al_{m^2-m^1}} = \frac{k+1}{k_1+1} = 1.0844;$$

$$\frac{D_1D_2}{A_1A_2} = \frac{\text{Incr. } Fe_{m^2-m^1}}{\text{Incr. } Al_{m^2-m^1}} = \frac{k+1}{k_1+1}(k_2+1) = 4.3604;$$

$$\frac{D_1D_2}{B_1B_2} = \frac{\text{Incr. } Fe_{m^2-m^1}}{\text{Incr. } V_{m^2-m^1}} = \frac{k_2+1}{k_1+1} = 1.3580.$$

Owing to the large errors introduced into the quotient of the observed solubility increments by variations of a few thousandths of a gram-molecule in the solubility determinations, we can expect only an approximate agreement between the above constants and their observed values. The latter, which, together with the variations from the calculated values (D), are given below, are therefore eminently satisfactory. The agreement between them is so marked that there can be no doubt as to the correctness of the law:

$$\frac{\text{Incr. } V_{m^2-m^1}}{\text{Incr. } Al_{m^2-m^1}} = 3.211. \qquad \frac{\text{Incr. } Cr_{m^2-m^1}}{\text{Incr. } V_{m^2-m^1}} = 0.3377.$$

m^2.	m^1.	Observed.	D.	Observed.	D.
NH_4	Cs	3.181	−0.030	0.3295	−0.0085
Tl	Cs	3.378	+0.167	0.3561	+0.0184
Rb	Cs	3.404	+0.193	0.4016	+0.0693
NH_4	Rb	3.149	−0.074	0.3185	−0.0192
Tl	Rb	3.356	+0.145	0.3384	+0.0007
NH_4	Tl	3.033	−0.178	0.3197	−0.0316

$$\frac{\text{Incr. } Fe_{m^2-m^1}}{\text{Incr. } Cr_{m^2-m^1}} = 4.021. \qquad \frac{\text{Incr. } Cr_{m^2-m^1}}{\text{Incr. } Al_{m^2-m^1}} = 1.084.$$

m^2.	m^1.	Observed.	D.	Observed.	D.
NH_4	Cs	4.118	+0.097	1.021	−0.063
Tl	Cs	3.829	−0.192	1.200	+0.116
Rb	Cs	3.957	+0.044	1.152	+0.068
NH_4	Rb	4.119	+0.098	1.003	−0.081
Tl	Rb	3.770	−0.250	1.127	+0.043
NH_4	Tl	4.410	+0.389	0.927	−0.159

$$\frac{\text{Incr. } Fe_{m^2-m^1}}{\text{Incr. } Al_{m^2-m^1}} = 4.360. \qquad \frac{\text{Incr. } Fe_{m^2-m^1}}{\text{Incr. } V_{m^2-m^1}} = 1.358.$$

m^2.	m^1.	Observed.	D.	Observed.	D.
NH_4	Cs	4.316	−0.044	1.357	−0.001
Tl	Cs	4.537	+0.177	1.363	+0.005
Rb	Cs	5.411	+1.051	1.606	+0.186
NH_4	Rb	4.164	−0.196	1.322	−0.031
Tl	Rb	4.280	−0.080	1.276	−0.067
NH_4	Tl	4.095	−0.265	1.350	−0.008

The only marked deviations from the calculated constants are in the case of $\frac{\text{Incr. } Cr_{Rb-Cs}}{\text{Incr. } V_{Rb-Cs}}$, where both increments are so small that even the slightest error of experiment has a great influence upon their ratio ; and in some of the ratios obtained with rubidium ferric alum. The observed solubility of this salt is probably somewhat high, owing to the readiness with which it undergoes hydrolysis. The error thus introduced, however, becomes very great only in the ratios $\frac{\text{Incr. } Fe_{Rb-Cs}}{\text{Incr. } M^{III}_{Rb-Cs}}$. In the ratios $\frac{\text{Incr. } Fe_{NH_4-Rb}}{\text{Incr. } M^{III}_{NH_4-Rb}}$ its influence is hardly felt.

The remaining variables of the triangles PBQ and SCQ, so far as their values are necessary for the derivation of a general formula for the solubilities, are also to be expressed in terms of θ_1 and k, k_1, etc.

If we call the angle of inclination of the base line PQ to the x-axis α, then for the variable angle BQP, or φ, we have the expression:

$$\tan \varphi = \frac{PB \sin (\theta - \alpha)}{PQ - PB \cos(\theta - \alpha)} = \frac{\rho (k+1) \sin (\vartheta - \alpha)}{PQ - \rho(k+1) \cos (\theta - \alpha)}.$$

In this formula, α and PQ are constant. Substituting for the latter and k their calculated values, we have

$$\tan \varphi = \frac{\rho \sin (\theta - \alpha)}{11.37 - \rho \cos (\theta - \alpha)} = \mathrm{R}.$$

Since $$B_1Q = \frac{B_1P \sin (\theta - \alpha)}{\sin \varphi},$$

the variable distance BQ becomes:

$$BQ = \frac{\rho(k+1) \sin (\theta - \alpha)}{\frac{\tan \varphi}{\sqrt{1 + \tan^2 \varphi}}}$$

$$= \frac{\rho(k+1) \sin (\theta - \alpha) \sqrt{1 + \mathrm{R}^2}}{\mathrm{R}} = M.$$

As the intercepts $BC = k_1 CQ$, and, therefore,

$$M = BC + \frac{BC}{k_1},$$

the relation which these intercepts bear to M are

$$BC = \frac{k_1 M}{k_1 + 1} \text{ and } CQ = \frac{M}{k_1 + 1}.$$

The base line SQ makes with the x-axis the constant angle β; the variable angle BQS is, therefore, $\varphi + \beta - \alpha$. For the angle DSQ, or Σ, we have, as in the case of the angle φ,

$$\tan \Sigma = \frac{CQ \sin (\varphi + \beta - \alpha)}{SQ - CQ \cos (\varphi + \beta - \alpha)}.$$

The value of α is 1°, 5′, 54″, and that of $\beta = 26°, 33', 54''$. Expanding and substituting for these and SQ their corresponding values, and for CQ its equivalent, $\frac{M}{k_1 + 1} = \frac{M}{2.9608}$, we have

$$\tan \Sigma = \frac{M(R + 0.4763)}{6.4011\sqrt{1 + R_2} - M(1 - 0.04763R)}.$$

The distance $AA_P = \rho \sin \theta$. The solubility of the aluminium alums is therefore expressed by the equation

$$S_{Al} = m + \rho \sin \theta, \qquad (1)$$

m being the y-value of the point P.

For the solubility of the vanadium alums we have

$$BB_P = BB_A + AA_P,$$

and since $BB_A = k\rho \sin \theta$, by addition with (1),

$$S_V = m + \rho \sin \theta + k\rho \sin \theta.$$

Passing in the same manner to the chromium alums,

$$CC_P = BB_P - BB_C$$
$$= BB_P - \frac{k_1 M}{k_1 + 1} \sin (\varphi - \alpha)$$

and, accordingly,

$$S_{Cr} = m + \rho \sin \theta + k\rho \sin \theta - \frac{k_1 M}{k_1 + 1} \sin (\varphi - \alpha). \quad (3)$$

The points D_1, D_2, etc., are expressed by

$$S_{Fe} = m + DD_P.$$
$$= m + DD_C + CC_P,$$

in which $DD_C = CD \sin (\Sigma + \beta)$.

The variable distance CD is given by the equation

$$CD = k_2 CS$$
$$= \frac{k_2 CQ \sin (\varphi + \beta - \alpha)}{\sin \Sigma}.$$
$$= \frac{k_2 M \sin (\varphi + \beta - \alpha)}{(k_1 + 1) \sin \Sigma}.$$

Substituting this value for CD, we have

$$S_{Fe} = m + CC_P + \frac{k_2 M \sin(\varphi + \beta - \alpha)}{(k_1 + 1)\sin \Sigma}(\sin \Sigma + \beta),$$

or,

$$S_{Fe} = m + \rho \sin \theta + k\rho \sin \theta - \frac{k_1 M}{k_1 + 1} \sin(\varphi - \alpha) + \frac{k_2 M \sin(\varphi + \beta - \alpha)}{(k_1 + 1)\sin \Sigma} \sin(\Sigma + \beta).$$

This also serves as a general formula for the solubility (S) of any of the sixteen alums taken into consideration. For if k_2 be made equal to zero, the last term falls away, having the equation in the forms applying to the chromium alums. With k_2 and k_1 equal to zero, the solubilities of the vanadium alums are obtained, and by eliminating the second term as well, those of the aluminium salts. We thus have a general solubility equation, all the terms of which can be referred to two variables: the one of these, θ, applying to the one class of elements in the compounds, the other, k, to the second class. I believe that aside from the instance of additive properties, which the solubilities certainly are not, this is the first case in which a mathematical relation between the corresponding properties of a class of compounds has been found capable of expression.

Below I give the values of θ and ρ for each of the alkali metals, and the solubilities as calculated by the general formula. With the latter, the column D contains the difference between the calculated and observed solubilities, and D' the variation from the values serving as a basis for the derivation of the constants:

	θ.	ρ.
Cs	2° 6′ 5″	10.945
Rb	27° 11′ 19″	12.254
Tl	57° 56′ 4″	20.5406
NH_4	73° 45′ 5″	38.943

In the following the solubilities are expressed in hundredths of a gram-molecule.

	Al.	D.	D'.	V. $k = 2.2110$.	D.	D'.	Cr. $k_1 = 1.9608$.	D.	D'.	Fe. $k_2 = 3.0213$.	D.	D.
Cs	1.192	−0.0108	−0.008	2.06	+0.02	−0.03	1.671	+0.160	−0.020	4.82	+0.32	−0.16
Rb	6.38	+0.328	−0.020	18.90	+1.20	+0.12	7.34	−0.36	0.00	27.76	−1.63	+0.06
Tl	18.21	+0.510	+0.010	56.70	−0.60	0.00	20.13	−1.07	−0.01	79.69	−0.30	+0.47
NH_4	38.18	+0.520	+0.020	120.82	− 0.08	−0.07	41.82	+1.12	0.00	165.26	−0.64	−1.17

In conclusion I may state that while the data now at hand are too few for accurate analysis, such determinations as I have made at temperatures other than 25° indicate that a general-solubility-formula for all temperatures will not be difficult of derivation. I have made determinations at 30° on the caesium, rubidium, and ammonium alums of aluminium, chromium, and iron, and find that the law of the constant ratio of the solubility-increments holds good at that temperature. The values of the constants k, k_1, and k_2, however, vary with the temperature. At 30° $\frac{\text{Incr. } Cr_{m^2-m^1}}{\text{Incr. } Al_{m^2-m^1}} = 1.2$ and $\frac{\text{Incr. } Fe_{m^2-m^1}}{\text{Incr. } Cr_{m^2-m^1}} =$ 8.3 in approximate numbers. From the fact that this law obtains at other temperatures, it necessarily follows that at these, as at 25°, the lines joining the solubility-points have common points of intersection. The same formula, therefore, with other constants, obtains at different temperatures. The mathematical relation between the solubilities at 25° can not, accordingly, be a matter of chance.

My thanks are due to Eugene Lamb Richards, Professor of Mathematics in Yale University, for many helpful suggestions embodied in this paper.

NEW HAVEN, April 30, 1901.

LXXXVI.—RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

BY HENRY L. WHEELER.

The treatment of ammonium or potassium thiocyanate with an alkyl halide, in every case which has been carefully examined, gives a normal thiocyanate, R.SCN, as the first product of the reaction. Whenever a mustard-oil is obtained it results from the molecular rearrangement of the normal thiocyanate first formed.

In the case of acyl halides, on the other hand, the products have the isomeric structure,[1] RCO—NCS, and the various chemists who have investigated this reaction have been un-

[1] Miquel: Ann. chim. phys., [5], **11**, 318 (1877). Dixon: J. Chem. Soc. (London), **67**, 565, 1040 (1895); **69**, 855, 1593 (1896); **71**, 617 (1897); **75**, 1388 (1899); **79**, 541 (1901). Doran: *Ibid.*, **69**, 328 (1896).

able to obtain any positive evidence of the intermediate formation of normal thiocyanates.

The theory generally accepted to account for the action of alkyl halides on potassium thiocyanate is that first proposed by Michael.[1] He assumes that the alkyl group combines with the sulphur and that then potassium halide separates so that a normal thiocyanate results as follows:

$$KSCN + C_2H_5I = K\overset{I}{\diagdown}\!\!\diagup\overset{C_2H_5}{}S\!-\!CN = C_2H_5.SCN + KI.$$

In another place[2] he mentions the possibility that halides may combine with the nitrogen in this salt. This would then permit of two distinct reactions leading to the formation of isothiocyanates, for he states that all compounds which contain the groups ROCN and RSCN, or ROCNH and RSCNH, will be transformed by heat into the isomeric compounds OC—NR and SCNR, or OCNHR and SCNHR.[3]

He states, as a self-evident fact, that this rearrangement will take place with greater difficulty, the more positive the hydrocarbon radical. As an example is cited the case of allyl thiocyanate,[4] which readily undergoes a molecular rearrangement even at ordinary temperatures, while methyl rhodanide requires heating to a high temperature[5] and the conversion into isothiocyanate, even then is not smooth.

Dixon remarks: "It would seem that the only halogenized compounds which undergo any material conversion into isothiocyanate are those in which the halogen is in direct combination with a negative group."

According to Frerichs and Beckurts[6] a number of chloracetyl derivatives, $ClCH_2CO.R$, $ClCH_2CO_2C_2H_5$, etc., give iso-

[1] J. prakt. Chem., **37**, 509 (1888).

[2] This JOURNAL, **14**, 486 (1892).

[3] In this connection it may be remarked that Victor Meyer was unable to transform ethyl thiocyanate by heat into the isothiocyanate—see Ann. Chem. (Liebig), **171**, 47 (1874)—and Wislicenus and Goldschmidt found that the imidoesters of Pinner decompose on heating alone—see Ber. d. chem. Ges., **33**, 1469 (1900)—although they readily suffer rearrangement when treated with alkyl halides. Cf. Wheeler and Johnson: This JOURNAL, **21**, 186 (1899); **23**, 135 (1900).

[4] Gerlich: Ann. Chem. (Liebig), **178**, 85 (1875).

[5] Hofmann: Ber. d. chem. Ges., **13**, 1350 (1880).

[6] Arch. d. Pharm., **237**, 286, 304 (1899); **238**, 9, 319, 615 (1900).

thiocyanates when treated with potassium thiocyanate. In a recent paper[1] from this laboratory it was shown that these supposed isothiocyanates are, without exception, normal thiocyanates.

Since, as far as has been observed, the influence of one —CO.R group (R = —OAlk., —NXY, $—CH_3$, $—C_6H_5$, $—C_4H_3S$ thiënyl, etc.) when introduced in place of hydrogen in methyl chloride, does not produce conditions favorable to the formation of isothiocyanates,[2] it seemed of interest to determine whether isothiocyanates would result when two or three of these negative groups are present. Experiments, which may be considered as preliminary to a wider examination of alkyl rhodanides, were undertaken with the following halides:

$ClCH(CO_2C_2H_5)_2$ I. $\qquad$ $ClC(CO_2C_2H_5)_3$ II.

Diethylchlormalonate (I) was found to react readily with alcoholic potassium thiocyanate, and the product could be boiled unaltered at reduced pressure. When heated with thiobenzoic acid it gave the diethylmalonate derivative of benzoyldithiocarbamic acid,

$$C_6H_5CO.NHCS.SCH(CO_2C_2H_5)_2,$$

a reaction which establishes the fact that this rhodanide is a normal thiocyanate.[3] This was further confirmed by boiling the rhodanide with concentrated hydrochloric acid, whereupon α-μ-diketotetrahydrothiazole, $\begin{matrix} S—CO \\ | \quad\quad \rangle NH \\ CH_2—CO \end{matrix}$, was obtained.

Tricarbethoxychlormethane (II) proved to be quite unreactive with alcoholic potassium thiocyanate, and little or no thiocyanate was obtained after boiling for a number of hours.[4]

[1] Wheeler and Merriam: J. Am. Chem. Soc., **23**, 283 (1901).

[2] According to Dixon, $ClCH_2—CO.OH$ gave an amount of "thiocarbimidic" product sufficient to be easily detected, although it was an insignificant fraction of the amount of acid used. J. Chem. Soc. (London), **65**, 390 (1899).

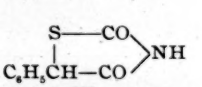
[3] Chanlaroff: Ber. d. chem. Ges., **15**, 1987 (1882); Wheeler and Merriam: *Loc. cit.*

[4] Diethyl ethylchlormalonate, $ClC(CO_2C_2H_5)_2C_2H_5$, also showed a noteworthy inertness. It did not react in alcoholic solutions with potassium thiocyanate, and no reaction was obtained on heating in benzene to 140° to 145° for a number of hours.

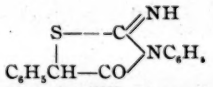
The effect produced by the presence of the negative phenyl group was then examined in the case of the following halides:

$ClCH(C_6H_5)CO_2C_2H_5$ (III.) $BrCH(C_6H_5)_2$ (IV.) $BrC(C_6H_5)_3$ (V.)

Ethyl phenylchloracetate (III), when boiled with alcoholic ammonium thiocyanate, gave an oil which distilled unaltered at reduced pressure. When this was heated with thiobenzoic acid it gave the ethyl phenylacetate derivative of benzoyldithiocarbamic acid, $C_6H_5CO.NHCS.SCH(C_6H_5)CO_2C_2H_5$, and therefore this rhodanide is a normal thiocyanate. In accordance with this it gives with hydrochloric acid α-μ-diketo-β-phenyltetrahydrothiazole (VI); and with amines, aniline, etc., it forms compounds which in all probability are pseudothiohydantoïns (VII):



VI.



VII.

When diphenylmethyl bromide (IV) is boiled in benzene solution with potassium thiocyanate, the crystalline product obtained undoubtedly has a mustard-oil structure,

$$(C_6H_5)_2CHNCS.$$

When this compound is heated with thiobenzoic acid, benzoylbenzhydrylamine, $C_6H_5CO.NHCH(C_6H_5)_2$, and carbon disulphide are formed. It reacts with ammonia and organic bases, in the cold, yielding diphenylmethylthioureas,

$$(C_6H_5)_2CH—NHCSNHR.$$

With concentrated sulphuric acid it gives benzhydrylamine, and it is readily desulphurized by boiling with alkaline lead solutions.

If diphenylmethyl bromide is allowed to react with ammonium thiocyanate at ordinary temperatures, in ether or benzene, an oil is obtained which shows no signs of solidifying until it is heated. On distilling at reduced pressure it readily solidifies. On treating the oil with sodium in alcohol, sodium

cyanide is formed in quantity, as shown by the Prussian-blue test. On the other hand, the solid product gives no sodium cyanide whatever, under the same conditions. This shows that a normal thiocyanate is the first product of the reaction and this undergoes a molecular rearrangement into the isothiocyanate, as in the case of allyl thiocyanate.

That triphenylmethyl bromide (V) forms a rhodanide has already been shown by Elbs.[1] Although he gives no data in regard to the structure of this rhodanide he shows that it is a very stable compound in regard to heat. He states that it distils at a high temperature without decomposition.

I have found that it reacts with thiobenzoic acid and forms triphenylmethyl thiolbenzoate, $C_6H_5CO.SC(C_6H_5)_3$, and with thioacetic acid it forms the analogous triphenylmethyl thiolacetate $CH_3CO.SC(C_6H_5)_3$. This reaction is characteristic of certain normal thiocyanates. For example, a precisely similar result was obtained with phenyl thiocyanate, C_6H_5SCN, which gave phenylthiolbenzoate,[2] $C_6H_5CO.SC_6H_5$.

In accordance with this, no thiourea derivatives were obtained by the action of ammonia or organic bases. Alcoholic ammonia gave triphenylmethyl amine, triphenylmethylethyl ether, triphenylmethyl carbinol, and ammonium thiocyanate. Moreover, this rhodanide is not desulphurized by boiling with an alkaline lead acetate solution and, on reducing in alcoholic solution with sodium, it responds to the Prussian blue test for cyanides. In other words, the entire behavior of this rhodanide is that of a normal thiocyanate.

It will be seen on comparing the above results that the facts are exactly opposite to what would be expected from the statement of Michael. The least negative or most positive of the above four halides which give rhodanides, forms an isothiocyanate with ease, while the others do not.

That the phenyl group has a less negative influence than the carbethoxy group is shown on substituting these groups in acetic acid and comparing the affinity-constants of the resulting acids:

[1] Ber. d. chem. Ges., **17**, 700 (1884).
[2] Wheeler and Merriam: *Loc. cit.*

CH_3COOH	$C_6H_5CH_2COOH$	$C_2H_5OCOCH_2COOH$
$K = 0.0018$[1]	$K = 0.00556$[1]	$K = 0.0451$[1]

The affinity-constant in the case of acetic acid is increased in the proportion of 1 : 3 by the introduction of the phenyl group, while by the more negative carbethoxy group it is increased in the proportion of 1 : 29.

That the phenyl group has a less negative influence than the carbethoxy group, in other compounds as well, is evident from a consideration of the properties of aniline and urethane.

From the fact that the affinity-constant of acrylic acid ($K = 0.0056$)[2] is somewhat smaller than that of benzoic acid ($K = 0.0060$)[2] it appears that the unsaturated group $CH_2=CH-$ has a less negative effect than the phenyl group. Nevertheless, allyl rhodanide suffers rearrangement with ease, while benzyl rhodanide, triphenylmethyl rhodanide, rhodanethyl acetate, and even rhodanethylmalonate do not.

The experimental evidence now brought forward goes to show that the tendency to form isothiocyanates is not proportional to the negative character of the radicals, and it will require further work to decide what influence determines the formation, or non-formation, of thiocyanates and isothiocyanates in the reactions in question. At present it is impossible to predict, in new cases, whether or not an alkyl rhodanide will undergo a molecular rearrangement.

EXPERIMENTAL PART.

Diethyl Thiocyanmalonate, $NCSCH(CO_2C_2H_5)_2$.—Diethyl chlormalonate reacts in the cold with an alcoholic solution of potassium thiocyanate. Forty grams of the ester were warmed with an excess of potassium thiocyanate for twenty minutes. On distilling off some of the alcohol and adding water, 40 grams of yellow-colored oil were obtained. Almost two-thirds of this boiled at 169° to 170° at 22 to 23 mm. pressure; a small amount distilled at 150° to 169°. It forms a colorless oil with very little odor, and a nitrogen determination gave:

[1] Ostwald: Ztschr. phys. Chem., **3**, 419 (1889); *Ibid.*, 270; Walker: J. Chem. Soc. (London), **61**, 711 (1892).

[2] Ostwald: *Loc. cit.*

	Calculated for $C_8H_{11}O_4NS$.	Found.
N	6.45	6.82

Five grams of this oil were evaporated to dryness with 15 cc. of concentrated hydrochloric acid. On allowing the residue to crystallize spontaneously from water, large, colorless, transparent, four-sided tables melting at 125° to 126° were obtained. A nitrogen determination gave 11.93 per cent. of nitrogen, while the amount calculated for α-μ-diketotetrahydrothiazole is 11.96 per cent.

Diethyl Malonate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCSSCH(CO_2C_2H_5)_2$.—Molecular quantities of the above rhodanide and thiobenzoic acid were warmed in benzene solution for about three hours. The benzene was then removed and the residue, which readily solidified, was purified by dissolving in dilute alkali and precipitating with hydrochloric acid. The small amount of material insoluble in alkali proved to be benzoyl disulphide. On crystallizing the precipitate produced by hydrochloric acid from alcohol, long, bright-yellow, flattened prisms or plates were obtained, melting at 119°. A nitrogen determination gave:

	Calculated for $C_{15}H_{17}O_5NS_2$.	Found.
N	3.94	3.84

The yellow color of this compound, its solubility in alkali, and the above analysis show that this is a benzoyldithiourethane.

Tricarbethoxychlormethane and Potassium Thiocyanate, 35 grams of the former and 15 grams of the latter, were boiled for two days in alcoholic solution. Some potassium chloride separated and the solution became yellow-colored. A portion of the alcohol was evaporated off and water then precipitated an oil, which boiled at 158° to 168° at 21 to 23 mm. pressure. On cooling, yellow needles separated which proved to be pure sulphur. The oil was redistilled at 29 mm. pressure, whereupon about one-half boiled at 163° to 166°. A nitrogen determination in this gave 1.75 per cent nitrogen, while the calculated amount for tricarbethoxymethyl rhodanide is 4.84 per

cent. The oil, which was found to contain chlorine, was then distilled at 140 mm. pressure, whereupon almost all boiled at 208° to 210°. This was, therefore, unaltered tricarbethoxychlormethane, which Conrad[1] states boils at 210° at the above pressure. The inertness of this ester and of diethyl ethylchlormalonate, already mentioned, in comparison with diethyl chlormalonate is noteworthy.

Ethyl Phenylchloracetate, $ClCH(C_6H_5)CO_2C_2H_5$.—Phenylchloracetylchloride was prepared from mandelic acid by the process of Bischoff, Walden.[2] This (77 grams) was poured into an excess of alcohol and then distilled at 18 to 17 mm. pressure, whereupon it practically all boiled at 142° to 145°. Out of a yield of 68 grams, 20 grams boiled at 142° and formed a colorless oil with a pleasant, fruity odor, the vapor of which has a slight irritating effect on the eyes. A chlorine determination gave :

	Calculated for $C_{10}H_{11}O_2Cl$.	Found.
Cl	17.88	17.96

Ethyl Phenylthiocyanacetate, $NCSCH(C_6H_5)CO_2C_2H_5$, resulted on warming the chloride for a few minutes with alcoholic ammonium thiocyanate. It forms an oil which distilled for the most part at 182° to 184° at 17 mm. pressure. A nitrogen determination gave :

	Calculated for $C_{11}H_{11}O_2NS$.	Found.
N	6.3	6.9

When 5 grams of this oil were treated with concentrated hydrochloric acid and evaporated to dryness and the residue crystallized from alcohol, beautiful colorless prisms were obtained, melting at 125° to 126°. A nitrogen determination agreed with the calculated amount for α-μ-diketo-β-phenyltetrahydrothiazole :

	Calculated for $C_9H_7O_2NS$.	Found.
N	7.25	7.24

This material is very soluble in alcohol and difficultly soluble in water. It dissolves in dilute alkali.

[1] Ber. d. chem. Ges., 14, 618 (1881).
Ann. Chem. (Liebig), 279, 122 (1894).

Diphenylpseudothiohydantoïn.—When 5 grams of the above thiocyanate were warmed on the water-bath with 2.1 grams of aniline for twelve hours a varnish was obtained which, on taking up in alcohol, deposited needles and plates. The latter, on crystallizing several times from alcohol, melted at 185° to 186°, and a nitrogen determination gave :

	Calculated for $C_{15}H_{13}ON_2S$.	Found.
N	10.4	10.2

The material is insoluble in cold alkali, but readily dissolves on warming. On boiling the solution no aniline could be detected in the distillate.

Ethyl Phenylacetate Derivative of Benzoyldithiocarbamic Acid, $C_6H_5CO.NHCS.SCH(C_6H_5)CO_2C_2H_5$.—Molecular quantities of the rhodanide and thiobenzoic acid were heated in benzene for several hours. On removing the benzene only a trace of carbon disulphide was found. The residue formed a varnish, which, on dissolving in dilute sodium hydroxide and precipitating with hydrochloric acid, gave a solid. This was crystallized from alcohol, in which it is readily soluble, whereupon a mass of thin, yellow plates were obtained, melting at 150° to 154°. A nitrogen determination gave :

	Calculated for $C_{18}H_{17}O_3NS_2$.	Found.
N	3.90	3.91

Diphenylmethyl Isothiocyanate, $(C_6H_5)_2CH—NCS$. — Diphenylmethyl bromide was prepared by the method of Friedel Balsohn.[1] This bromide immediately reacts with an alcoholic solution of ammonium or potassium thiocyanate. The product is an oil, apparently containing some diphenylmethylethyl ether. On distilling at 38 to 37 mm. pressure a portion boils below 222°, then the greater part at 222° to 225°. The latter distillate forms a blue liquid which, on cooling, solidifies. On crystallizing from alcohol it melts at 61° and forms beautiful colorless prisms. It is best prepared by boiling a benzene solution of the bromide with finely powdered ammonium or potassium thiocyanate for several days. When an

[1] Bull. soc. chim. (Paris), **33**, 339.

ether solution of the bromide, free from alcohol, is allowed to stand over potassium thiocyanate for a number of days the product is an oil which consists for the most part of normal diphenylmethyl thiocyanate, since on reduction with sodium it gives sodium cyanide. An analysis of the material crystallized from alcohol and melting at 61° gave :

	Calculated for $C_{14}H_{11}NS$.	Found.
N	6.22	6.43

When this material is boiled with alkaline lead acetate it is desulphurized. No sodium cyanide was obtained when this was reduced in alcohol by sodium.

Diphenylmethylacetamide, $CH_3CO—NHCH(C_6H_5)_2$, was formed when 1.5 grams of the isothiocyanate, 3 grams of thioacetic acid, and 10 cc. of benzene were warmed for an hour on the steam-bath. Carbon disulphide was then identified by means of the xanthate test and the residue was crystallized from dilute alcohol, whereupon the material formed a felted mass of colorless needles melting at 146° to 147°. It is very soluble in strong alcohol, from which it crystallizes in the form of compact prisms. A nitrogen determination gave :

	Calculated for $C_{15}H_{15}ON$.	Found.
N	6.22	6.51

This amide is easily saponified by warming with concentrated hydrochloric acid. The long colorless needles thus obtained melt at 270° (benzhydrylamine hydrochloride).

Diphenylmethylbenzamide, $C_6H_5CONH.CH(C_6H_5)_2$, was formed when 4.4 grams of the isothiocyanate, 2.7 grams of thiobenzoic acid, and 10 cc. of benzene were warmed for several hours. On evaporating the benzene, carbon disulphide was found in quantity, and, on crystallizing the residue from alcohol, colorless, silky needles were obtained, melting at 166° to 167°. A nitrogen determination in the sulphur-free material gave :

	Calculated for $C_{20}H_{17}ON$.	Found.
N	4.87	5.21

This amide may be boiled for days with alkali without any apparent saponification. On boiling for a number of days with alcohol and concentrated hydrochloric acid a small amount of benzhydrylamine hydrochloride was obtained, melting, as Leuckart and Bach[1] state, at 270°.

Diphenylmethylthiourea, $(C_6H_5)_2CH—NHCSNH_2$. — One gram of the isothiocyanate was dissolved in alcoholic ammonia, whereupon, on standing over night, beautiful, long, colorless, silky needles separated, melting at 189°. This urea is readily soluble in hot alcohol, and a nitrogen determination gave :

	Calculated for $C_{14}H_{14}N_2S$.	Found.
N	11.5	11.3

Diphenylmethyl-methylthiourea, $(C_6H_5)_2CH—NHCSNHCH_3$. —Two grams of the isothiocyanate were dissolved in alcohol and a 33 per cent solution of methyl amine was added in excess, whereupon an almost immediate separation of colorless, flattened prisms took place. On crystallizing from alcohol they melted at about 152°, and a nitrogen determination gave :

	Calculated for $C_{15}H_{16}N_2S$.	Found.
N	10.9	10.7

This material is easily soluble in alcohol.

Diphenylmethyl-diethylthiourea, $(C_6H_5)_2CH—NHCSN(C_2H_5)_2$, from the isothiocyanate and diethylamine, forms colorless needles, readily soluble in hot alcohol and melting at 112° to 113°. A nitrogen determination gave :

	Calculated for $C_{18}H_{22}N_2S$.	Found.
N	9.39	9.35

Diphenylmethyl-diisobutylthiourea, $(C_6H_5)_2CH—NHCSN(C_4H_9)_2$. — Diisobutylamine combines with the isothiocyanate with evolution of heat, and, on cooling, the material solidifies to a radiating mass of crystals. It forms long, colorless needles from alcohol, which melt at 97° to 98°. A nitrogen determination gave :

[1] Ber. d. chem. Ges., **19**, 2129 (1886).

	Calculated for $C_{21}H_{20}N_2S$.	Found.
N	7.90	8.33

This material is insoluble in alkali, and alkaline lead acetate solutions produce no blackening on boiling.

Diphenylmethylphenylthiourea, $(C_6H_5)_2CH—NH—CSNHC_6H_5$.—The isothiocyanate reacts readily with aniline, when gently warmed, and the mixture solidifies to a white powder. It is very difficultly soluble in alcohol. For analysis it was crystallized from a mixture of toluene and ethyl benzoate; it then melted at 178°. On recrystallizing from glacial acetic acid the melting-point was not altered, and a nitrogen determination gave:

	Calculated for $C_{20}H_{18}N_2S$.	Found.
N	8.80	8.79

It forms a sandy powder which appears to consist of small, compact, colorless prisms. This thiourea has been prepared from diphenylmethylamine and phenylisothiocyanate by Michaelis Linow,[1] who gives its melting-point as 180°.5.

Diphenylmethyl-methylphenylthiourea, $(C_6H_5)_2CH—NH—CS—N(CH_3)C_6H_5$, forms beautiful, long, colorless, slender needles when crystallized from alcohol. It melts at 119° to 120°, and a nitrogen determination gave:

	Calculated for $C_{21}H_{20}N_2S$.	Found.
N	8.43	8.63

Diphenylmethyl-β-naphthylthiourea, $(C_6H_5)_2CH—NHCSNHC_{10}H_7$, forms colorless needles melting at 179°. A nitrogen determination gave:

	Calculated for $C_{24}H_{20}N_2S$.	Found.
N	7.60	7.55

Diphenylmethyl-phenylthiosemicarbazide, $(C_6H_5)_2CH.NHCS(C_6H_5)N—NH_2$.—The isothiocyanate combines smoothly in alcoholic solution with phenylhydrazine. The product is difficultly soluble in alcohol but crystallizes from a mixture of alcohol and ethylbenzoate in colorless

[1] Ber. d. chem. Ges., 26, 2170 (1893).

plates which melt at 178°. A nitrogen determination gave :

	Calculated for $C_{20}H_{18}N_2S$.	Found.
N	12.65	12.62

This product exhibits the curious behavior observed by Marckwald[1] in the case of diphenylthiosemicarbazide, of having two melting-points. If the temperature is maintained at 178°, or a little above, the substance melts completely, but in a few seconds it solidifies and then melts at 198° with effervescence and decomposition. In all probability this behavior is due to a molecular rearrangement in the sense discussed by Busch and Holzmann :[2]

$$\underset{\text{Melting-point 178°.}}{(C_6H_5)_2CHNHCS(C_6H_5)N{-}NH_2} \rightarrow \underset{\text{Melting-point 198°.}}{(C_6H_5)_2CH{-}NHCSNH{-}NHC_6H_5.}$$

Triphenylmethyl Thiolacetate, $CH_3CO.SC(C_6H_5)_3$. — Six grams of triphenylmethylrhodanide[3] and 5 grams of thioacetic acid were heated in 20 cc. of benzene for ten hours. A small amount of carbon disulphide was formed. The residue, on evaporating the benzene, solidified. It was crystallized from alcohol, whereupon beautiful, colorless, twinned prisms were obtained, melting at 138° to 140°. A sulphur determination gave :

	Calculated for $C_{21}H_{18}OS$.	Found.
S	10.06	10.03

Triphenylmethyl Thiolbenzoate, $C_6H_5COSC(C_6H_5)_3$.—Four grams of the rhodanide and 1.9 grams of thiobenzoic acid were heated in 20 cc. of benzene for a number of hours. Carbon disulphide was formed and, on evaporating the benzene, a residue very difficultly soluble in alcohol was obtained. It was readily soluble in benzene and crystallized from a mixture of benzene and chloroform in colorless prisms, melting at 184° to 185°. A sulphur determination gave :

	Calculated for $C_{26}H_{20}OS$.	Found.
S	8.4	8.5

[1] Ber. d. chem. Ges., **25**, 3098 (1892).
[2] *Ibid.*, **34**, 320 (1901).
[3] *Ibid.*, **17**, 700 (1884).

It was found that this compound could be prepared from potassium thiolbenzoate and triphenylmethyl bromide, a fact that thoroughly establishes its identity.

Triphenylmethyl Thiocyanate and Ammonia.—The rhodanide (10 grams) was dissolved in benzene and this solution was mixed with an excess of alcoholic ammonia and allowed to stand for three days. At the end of this time it was evaporated to dryness and the residue was extracted with hot water. The undissolved residue was then dissolved in benzene, dried, and saturated with dry hydrochloric acid, whereupon triphenylmethylamine hydrochloride separated in the form of small plates, melting at 244°[1] (2.7 grams). The benzene solution was evaporated to dryness and the residue (4.6 grams) proved to be triphenylmethylethyl ether, which crystallizes from alcohol in beautiful stout prisms melting at 83° to 84°.

The aqueous extract, on evaporating almost to dryness, left a flocculent precipitate (1 gram) which, on crystallizing from alcohol, melted at 159°. It was free from sulphur and proved to be triphenylmethylcarbinol. The filtrate from this gave 2 grams of ammonium thiocyanate, calculated 2.4 grams. There was, therefore, no evidence of the formation of a thiourea derivative.

Triphenylmethyl Thiocyanate and aniline gave a mixture of substances from which phenylthiourea was the only material isolated in a state of purity.

Triphenylmethyl Thiocyanate and Phenylhydrazine, when warmed in alcohol, gave colorless prisms melting with effervescence at 201°. A nitrogen determination agreed with the calculated figure for phenylthiosemicarbazide: found, 25.30; calculated, 25.15. Besides this, the unstable triphenylmethanehydrazobenzene described by Gomberg[2] appears to be formed.

In a preliminary experiment, where the substances were mixed at random in order to determine whether they would react, a product was obtained crystallizing in prisms like

[1] Elbs: *Loc. cit.*

[2] Ber. d. chem. Ges., **30**, 2045 (1897).

phenylthiosemicarbazide, but which, after three crystallizations from alcohol, appeared to melt constantly at about 137° (with effervescence). A nitrogen determination in this material gave 10.4 per cent, while the calculated amount for triphenylmethyl-phenylthiosemicarbazide is 10.2 per cent. The writer believes that this product was in all probability a mixture, since subsequent attempts to obtain material in this reaction melting constantly at 137° were without success.

The reactions of triphenylmethylrhodanide with thiol acids appear to leave no doubt that the compound is a normal thiocyanate. Theoretically, a compound that easily separates the —NCS group might possibly act as follows:

$$(C_6H_5)_3C—\boxed{NCS\ \ H}SCOCH_3 = (C_6H_5)_3CS.COCH_3 + HNCS.$$

But this reaction has not yet been observed in the case of mustard oils. The invariable reaction is a separation of carbon disulphide and formation of a substituted acid amide. Even benzoyl isothiocyanate, which easily parts with the —NCS group, under certain conditions, with thiobenzoic acid gives dibenzamide.

The action of bases on triphenylmethyl rhodanide is according to what would be expected if the compound had the structure of a normal thiocyanate. But here again, according to Dixon, negative isothiocyanates, CH_3CONCS, are capable of behaving in this manner.

It is noteworthy in this connection that Hemilian and Silberstein[1] were unable to prepare any ureas either from triphenylmethylamine hydrochloride and potassium cyanate or from the base and carbon disulphide.

However, all the experimental evidence thus far obtained points to the curious fact that triphenylmethyl bromide forms a normal thiocyanate, while, not only on account of its negative character but also from analogy with diphenylmethyl bromide, it should form an isothiocyanate.

The following experiments by Dr. T. B. Johnson illustrate some new reactions of strongly negative isothiocyanates. It was found by qualitative experiments that benzoylisothiocyanate

[1] Ber. d. chem. Ges., 17, 742 (1884).

reacts with sodium malonic ester, sodium formanilide, sodium phenolate, and sodium acetoacetic ester, and in each case the —NCS group was removed as sodium thiocyanate. In these reactions, as with water, the isothiocyanate appears to act like an acyl halide. Phenyl isocyanate, on the other hand, combines with the sodium salts of certain compounds while the free substances do not react.[1]

It seemed of interest to determine whether benzoyl rhodanide would behave as a mustard-oil towards phenol ethers, etc., in the presence of aluminium chloride.[2] The action, as perhaps might be expected, was far from satisfactory in regard to smoothness. In one case—with toluene—we obtained a compound which crystallized from alcohol in red prisms and was soluble in alkali. It melted at 135° to 136°, and a nitrogen determination gave 5.64 per cent of nitrogen while the calculated figure for

$$CH_3C_6H_4.CSNHCOC_6H_5 = C_{15}H_{13}ONS$$

is 5.5 per cent.

In the case of phenetol the product proved to be paraethoxythiobenzamide, which formed plates from benzene melting at 158°. Analysis gave 7.95 per cent of nitrogen while the calculated amount for $C_2H_5—OC_6H_4CSNH_2 = C_9H_{11}ONS$ is 7.73 per cent.

It was also established that benzoyl isothiocyanate combines with hydrogen phosphide, apparently to form the phosphourea $C_6H_5CO.NHCSPH_2$. This was obtained as an orange-colored precipitate which dissolved in alkali, forming a red solution. It was very soluble in alcohol but difficultly soluble in benzene. It melted at about 155° to 157°, and a nitrogen determination gave 7.02 per cent of nitrogen, while the calculated amount for C_9H_9ONPS is 7.10 per cent.

NEW HAVEN, CONN., May 22, 1901.

[1] Paal: Ber. d. chem. Ges., **27**, 974 (1894); Fischer: *Ibid.*, **33**, 1701 (1900).
[2] Gattermann: Ber. d. chem. Ges., **25**, 3525, 3528 (1892).

PHENOXOZONE DERIVATIVES.

By H. W. Hillyer.

As indicated in a previous paper,[1] when one molecular proportion of picryl chloride, one of pyrocatechin, and two of sodium ethylate, are heated to from 60° to 70° a reaction takes place according to the following equation,

$$C_6H_4(OH)_2 + C_6H_2Cl(NO_2)_3 = C_6H_4O_2C_6H_2(NO_2)_2 + HNO_2 + HCl,$$

and results in the formation of a dinitro derivative of diphenylene dioxide or phenoxozone. The reaction has since been farther studied, and it has been found that in this particular case the yield is not greatly diminished by using alcoholic sodium hydroxide instead of sodium ethylate, and by reducing the relative amount of alcohol used as a solvent. In one case the reaction was carried through in the following manner: 60 grams of picryl chloride and 26 grams pyrocatechin were covered with 1 liter of common alcohol, heated until the picryl chloride was dissolved, and to the mixture a solution of 19.2 grams of sodium hydroxide in a small quantity of water was added. After heating for about four hours, to about 70°, the dinitrophenoxozone precipitated out was filtered off and washed free from the dark impurity present with water and alcohol. When air-dried, the crude substance weighed 50 grams, or 75 per cent of the theoretical.

Acetone is found to be a better solvent than glacial acetic acid or benzene. By dissolving in as little hot acetone as possible about 75 per cent of that dissolved is reprecipitated on cooling.

Reduction with Zinc and Acetic Acid.—On reducing a solution of the substance in glacial acetic acid with zinc dust, a solution is obtained which is colorless, but, on diluting and filtering, the solution becomes wine-red. Ether extracts the colored substance from the dilute acetic acid solution. When the ether solution is shaken with hydrochloric acid it becomes

[1] This Journal, 23, 125.

colorless, but on adding sodium acetate the ether again becomes colored. This seems to indicate that a color-base is present whose hydrochloric acid salt is not decomposed by water, while its acetate is hydrolyzed in such a manner that the base can be extracted with ether. The base formed by reduction cannot readily be isolated, but, as appears from work described later, it seems at least probable that one of the oxygen linkages of the phenoxozone is hydrolyzed at the same time that a reduction is effected. The oxidized acetic acid solution is capable of dyeing silk to a dove color. When the solution, immediately after the reduction, is run into a solution of diazotized sulphanilic acid, the mixture turns brown, and on adding sodium hydroxide and common salt, a brick-red precipitate is formed which may be filtered off. It dissolves with difficulty in cold water, but quite easily in hot water, and, on cooling, separates again as a red powder. Its solutions dye silk brown. The reduction with zinc and acetic acid was here abandoned, since it was found that a clean reduction could be effected by the use of tin and hydrochloric acid.

Diamidophenoxozone.—Ten grams of finely pulverized dinitrophenoxozone are covered with about 150 cc. concentrated hydrochloric acid. Granulated tin is then added. The yellow substance gradually goes into solution, especially on heating on the water-bath. When the nitro compound has nearly all disappeared, the contents of the flask, on cooling, becomes a thick magma of colorless crystals. On adding much water the crystals dissolve. An excess of sodium hydroxide added to the filtered solution precipitates a base along with some tin compounds. The solution is filtered through glass-wool and the precipitate is slightly washed with water. The precipitate is boiled with about 500 cc. of alcohol and filtered. On cooling, the base separates in thin white or light-pink needles, which pack together like felt on filtering. After drying, the first crop of crystals weighs about 5 grams. When the mother-liquor is evaporated to about 200 cc., crystals again begin to separate and, on cooling, a further deposit of crystals may be obtained, especially on adding water to the alcoholic solution.

When equal quantities of alcohol and concentrated hydrochloric acid are used, instead of pure acid, the reduction takes place more quickly, but the base, as purified above, is of a violet-brown color, and crystallizes in thin scales composed of needles laid side by side. They have the same final melting-point as the needles above described, but melt less sharply. The base prepared in this way can be purified by adding stannic chloride and precipitating the tin as sulphide. The sulphide carries down the impurities and the base from the filtered solution is identical with that obtained above. The base melts with blackening at 198° to 200°. A nitrogen determination showed the substance to be diamidophenoxozone.

	Calculated for $C_6H_4O_2.C_6H_3(NH_2)_2$.	Found.
N	13.08	13.17

As a metadiamine it is difficult to diazotize. When nitrite is added to its acidified solution it yields a brown dye-stuff, having the same general color as Bismarck-brown.

A portion of the diamido compound was dissolved in dilute hydrochloric acid. Hydrochloroplatinic acid was added to this solution and produced a whitish precipitate which, when warmed, went into solution, but failed to separate again on cooling, on account of a probable decomposition. Gold chloride gave a greenish precipitate, but on warming there was evident decomposition. To a new portion of the hydrochloride hydrochlorplatinic acid was added, the precipitate filtered off and washed with water, alcohol, and ether. The precipitate is changed by the washing to an orange-brown substance. A part of this latter was air-dried and analyzed by ignition. The analyses are not concordant, but on the whole show that enough hydrochlorplatinic acid is removed by the washing to leave a salt in which the base acts as a monacid base.

	Calculated for $[C_6H_4O_2C_6H_3(NH_2)_2]_2H_2PtCl_4$.	Found. I.	II.	III.	IV.
Pt	23.2	23.2	24.1	27.1	27.4

By dissolving the base in absolute alcohol and precipitating with an absolute alcoholic solution of hydrochlorplatinic acid

and washing with absolute alcohol a salt was obtained, having as high a percentage as is demanded by theory for a compound in which the base acts as a diacid base.

	Calculated for $[C_6H_4O_2C_2H_3(NH_3)_2]H_2PtCl_6$.	Found. I.	II.
Pt	31.2	28.8	31.4
		28.9	30.5
		....	30.4

These results show the weakly basic character of one of the amido groups.

Diacetyldiamidophenoxozone.—About 5 grams of 1.3-diamidophenoxozone and 25 cc. glacial acetic acid were heated to boiling for four or five hours with no apparent change, but on distilling off about 10 cc. of the acid a decided reaction set in and the mass became solid and not easily soluble on adding more acetic acid. The substance was purified by washing with water and recrystallizing from ethyl acetate to which a little alcohol was added to increase the solubility. The product crystallizes from this solvent in very small, pearly-white, glistening scales, which, when filtered, form a mass in the filter which greatly resembles white paper, the different layers added by each filling of the funnel being easily separable when the substance is dry. The crystals melt with blackening at 252°.5 to 253°.

	Calculated for the diacetyl compound.	Found. I.	II.
C	64.4	64.2	64.7
H	4.69	4.69	5.1
N	9.4	8.8	9.0

The amido compound dissolves in dilute sulphuric acid if heat is applied, but on cooling crystals separate. Recrystallization gives radial masses of slender needles of a pale-pink color.

Benzoyldiamidophenoxozone.—From diamidophenoxozone the benzoyl derivative was made by the Schotten-Baumann reaction. The pasty mass first formed, on being treated with alcohol, was disintegrated and left a white powder insoluble even in hot alcohol. The powder was filtered off and a

solvent sought for. It is not perceptibly soluble in benzene, toluene, ether, petroleum ether, ethyl acetate, or alcohol at boiling temperatures. It is slightly soluble in boiling amyl alcohol, but can be best purified by dissolving it in hot nitro benzene, from which it separates, on cooling, in a fine powder. After crystallizing twice from nitrobenzene and washing with alcohol the substance melts at 274° to 275°.

Action of Alkali on Dinitrophenoxozone.—When 1,3-dinitrophenoxozone is treated with an alcoholic solution of sodium ethylate, it dissolves with a beautiful carmine color. On adding water, a yellow precipitate is formed insoluble in dilute aqueous alkalies and in alcohol. It has the melting-point and appearance of the original dinitrophenoxozone. The colored solution probably contains an addition-product like that described by Hantzsch.[1]

If instead of sodium ethylate a solution of sodium hydroxide in aqueous alcohol is used, the dinitrophenoxozone easily dissolves, but the resulting compound is different. An alcoholic solution of sodium hydroxide was poured upon 14.7 grams of the dinitro compound. On warming the solution the powder was easily dissolved. Water produces no precipitate. On adding hydrochloric acid to the orange aqueous alcoholic solution a light-yellow substance is precipitated which soon collects in crystals. These can be recrystallized from 50 per cent alcohol, in which the substance is freely soluble in the heat but only slightly soluble in the cold. The product was 14.9 grams.

The substance is very little soluble in cold water and only sparingly soluble in hot water. It melts at 153° to 153°.5. In water solution it slowly reddens blue litmus paper. It slowly dissolves in a cold solution of sodium carbonate, but on warming the solution it dissolves more rapidly with evolution of carbon dioxide. It dissolves slowly in a solution of sodium acetate, coloring it yellow. From its solution in alkali it is not precipitated by acetic acid, though the orange color of the solution is changed to yellow. On adding hydrochloric acid to this yellow solution the substance separates in crystalline

[1] Ber. d. chem. Ges., **32**, 3137.

flocks. These qualitative reactions point to the presence of a dioxynitrophenol with one hydroxyl group much more strongly acidic than the other. Analysis of the substance yields the following results:

	Calculated for $(HO)C_6H_4OC_6H_2(NO_2)_2(OH)$.	Found. I.	Found. II.
C	49.3	49.02	49.1
H	2.74	2.94	2.99

The substance is dioxydinitrophenoxide formed by the hydrolysis of one of the oxygen bonds of the dinitrophenoxozone,

$$C_6H_4O_3C_6H_2(NO_2)_2 + 2NaOH = (NaO)C_6H_4OC_6H_2(NO_2)_2ONa + H_2O.$$

Which of the oxygen bonds is hydrolyzed, or whether, in spite of the sharp melting-point, we have both of the isomeric substances possible cannot now be settled. Argument from analogy is not at all certain in its indications in this case.

The dioxydinitrophenoxide dissolves in ammonia water with considerable ease when the solution is warmed. After boiling until the odor of ammonia is no longer perceptible, the solution, on cooling, deposits long yellow needles in radial masses. They are crystals of the ammonium salt and, on treatment with a solution of sodium hydroxide, they yield ammonia.

The nitrophenol, when treated with an excess of strong solution of sodium hydroxide, yields a garnet-red solution and a crystalline-red precipitate. By filtering this precipitate from the alkaline solution by means of a small Puckal filter and recrystallizing from a small amount of hot water, garnet-red crystal aggregates of a rhombic shape separate. The mother-liquor from the recrystallized substance, on evaporation, deposits stout, light-orange crystals, which are apparently monoclinic and frequently twinned. They soon effloresce on exposure to the air. When dioxydinitrophenoxide is dissolved with two molecular equivalents of sodium hydroxide and the solution evaporated to the point of crystallization, two kinds of crystals like those above separate at the same time: first, garnet-red, rhombic aggregates; secondly, orange-red, six-

sided, apparently monoclinic crystals. The latter, on standing in the air, effloresce, and in effloresing show a strong tendency to cleave parallel to the crystal faces, especially parallel to the clinopinacoid. The two kinds of crystals can be separated by sifting, after efflorescence of the second kind. The latter, dissolved in hot water, crystallizes out on cooling the solution sometimes in the original form, but more often in orange-yellow needles. These needles do not lose weight when heated to 110° to 115°. Analysis to determine the sodium is difficult on account of the vigor of the reaction when the salt is heated with sulphuric acid.

	Calculated for monosodium salt.	Found. I.	II.	III.
Na	7.3	6.40	6.85	6.75

In another experiment a slight excess of alkali was used, and, on evaporating, there was a deposit of the dark rhombic aggregates, and mixed with them an equal quantity of stout, well-formed, ruby-colored crystals with well developed crystal faces. The latter do not effloresce. Separated by hand and recrystallized, each of these deposits, first a little of the other kind, and then from the mother-liquor a crop of the kind selected.

The ruby crystals, on drying over sulphuric acid *in vacuo*, lose nearly 1 molecule out of the three molecules of water of crystallization and yield, on evaporation with sulphuric acid, an amount of sodium sulphate confirming the theory, though not very closely agreeing with it.

	Calculated for sodium salt + $3H_2O$.	Found. I.	II.
H_2O	4.6	4.49	4.33
Na_2	11.79	11.99	11.05

The recrystallized garnet salt appears in massive crystals of the color of potassium ferricyanide. These, over sulphuric acid *in vacuo*, lose 4.23 and 4.52 per cent.

On heating in an air-bath from 110° to 115° more weight was lost, amounting with that *in vacuo* to 11.3 per cent (calculated for $3H_2O$, 13.8 per cent), and on heating with sulphuric acid the amount of sodium sulphate indicates that the sodium salt has the composition below :

	Calculated for Na_2 in salt + $3H_2O$.	Found.
Na	13.8	10.93

On account of a lack of material these results could not be made more satisfactory, but they seem to show that the garnet salt is like the ruby salt, with perhaps an admixture of the monosodium salt. The nitrophenol, whether set free from the ruby salt, from the garnet salt, or from the needles of the monosodium salt, always has the same melting-point.

When dinitrodioxyphenoxide is treated with an amount of sodium hydroxide, just insufficient to dissolve it, a yellow solution is obtained, and, on evaporating to a small bulk, orange needles separate in tufts. When removed from the mother-liquor and allowed to dry in the air, and more quickly over sulphuric acid, they turn bright scarlet, probably from loss of water. Silver nitrate in excess was added to a solution of this salt, a yellow amorphous precipitate was formed, and immediately filtered off and washed slightly. On drying, the yellow silver salt changed to a brilliant scarlet and yielded, on analysis :

	Calculated for the mono-silver salt.	Found. I.	II.
Ag	27.06	27.3	27.6

Dioxydinitrophenoxide and zinc oxide mutually dissolve one another when covered with water to yield an orange solution, from which, through an accident, the zinc salt was not isolated.

The dimethyl compound of the nitrophenol was made by the method of Lander.[1] In a 250 cc. flask 4 grams of the phenoxide was treated with 8 grams silver oxide, 15 grams methyl iodide, and about 50 cc. benzene. After the first slight spontaneous action was over, the mixture was heated on the water-bath for about an hour It turned yellow in consequence of the formation of silver iodide. After driving off the excess of benzene, the residue was extracted with boiling alcohol, and from this, on cooling, a solid separates not soluble in a dilute, cold solution of sodium hydroxide, either aqueous or alco-

[1] J. Chem. Soc. (London), 1900, 729.

holic. When heated, however, it dissolves to yield a yellow solution, and with cold concentrated alcoholic soda it yields a solution of a fine carmine color. After crystallizing three times from hot alcohol the substance melts at 119° to 120°. This substance will be further studied.

When the dioxydinitrophenoxide is treated with tin and hydrochloric acid it is reduced, but when an attempt is made to isolate the base by precipitating the tin with hydrogen sulphide and treating the filtrate from this with an alkali, the solution turns violet and no base can be isolated. The hydrochloride can be obtained as a light violet mass by evaporating its solution in an atmosphere of hydrogen sulphide. The instability of the base and its turning violet strongly suggest the compound obtained when dinitrophenoxozone is reduced with zinc and acetic acid and also suggests the possibility that, in the latter case, the reduction may have been accompanied by a hydrolysis of one of the oxygen bonds.

In attempting to generalize the reaction described above, the following facts have been gathered : Under the conditions used above, picryl chloride and alkali, with alizarine, do not produce a condensation-product. No attempt has yet been made to bring about the change at a higher temperature.

Nitroparadibrombenzene, when treated with one molecular proportion of pyrocatechin and two molecular proportions of sodium hydroxide in alcoholic solution, yields no nitrite or workable product.

When dinitrobrombenzene (Br,NO_2,NO_2 : 1,2,4) is treated in the same way with pyrocatechin and alkali, it yields no nitrite but a considerable quantity of the ethyl ether of dinitrophenol (m. p. 84° to 85°). In this case the action takes place more readily with the alcohol present than with the pyrocatechin.

Successful attempts to bring about condensations similar to the first described have so far been made in two other cases. Nitropyrocatechin (OH,OH,NO_2 : 1,2,3), made by the action of an ethereal solution of nitric acid on an ethereal solution of pyrocatechin and subsequent steam distillation, yields with picryl chloride a condensation-product. A nitrite is formed

and a product is obtained consisting of yellow crystals. Further study of this compound was interruptedby the departure from the University of the student having it in charge.

Picryl chloride and alkali act readily on pyrogallol with the formation of much nitrite and chloride, but the isolation of the compound shows much difficulty. Using common alcohol and sodium hydroxide as the condensing agents, only a very small quantity of the desired product could be obtained, the greater part of the picryl chloride being changed to sodium chloride and sodium picrate, but, by the use of sodium alcoholate in absolute alcohol, a more satisfactory yield was obtained. In its final form the process was as follows: 10 grams picryl chloride and 5 grams pyrogallol were dissolved in 200 cc. hot absolute alcohol which had been redistilled from sodium. This, after the addition of 0.92 gram of sodium dissolved in from 40 to 50 cc. absolute alcohol, was heated one-half hour on the water-bath; a second portion of 0.92 gram of sodium in 40 cc. alcohol was then added and the whole heated from five to six hours. On adding the first portion of sodium a slight brownish precipitate separated, which proved to be mainly sodium chloride. On adding a second portion a heavy precipitate, chiefly of sodium nitrite, came down. The precipitate was filtered off, the filtrate evaporated to dryness, the residue washed with hot water several times and crystallized from acetone, and then several times from glacial acetic acid. From acetone it comes down in the form of a light-yellow powder; from acetic acid as broad, brown, transparent spikes, collected in tufts. The melting-point of the substance, crystallized three times from acetic acid, is 258° to 258°.5 with decomposition.

It is insoluble in cold water, sparingly soluble in hot water, benzene, and ether, more soluble in absolute alcohol, phenol, and ethyl acetate, and very soluble in nitrobenzene, glacial acetic acid, and acetone. It is soluble in dilute alkalies and reprecipitated from them unchanged by the addition of an acid, but in strong alkali it is decomposed, slowly in the cold and rapidly with heat, giving a dark-brown solution from

which a tarry mass is precipitated by a strong acid. The first analyses were made with some of the substance crystallized but twice from acetic acid. The crystals were washed with alcohol and dried in an air-bath at 150° for two hours. The first two combustions were lost in consequence of explosions. This was avoided in the other cases by mixing the substance with powdered copper oxide. The result of combustion I. not being very satisfactory, the substance was crystallized a third time and analyses II. and III. made.

	Calculated for $C_6H_3(OH)—O_2—C_6H_3(NO_2)_2$.	Found. I.	II.	III.
C	49.65	49.4	49.42	....
H	2.07	2.49	2.07	....
N	9.65	....	....	9.53

In view of these analytical results and of the fact that chloride and nitrite were formed and from the phenol-like character of the resulting compound in its conduct toward dilute alkali, the reaction seems to have taken place normally and to have resulted in the formation of a hydroxydinitrophenoxozone.

Two isomeric substances may, according to theory, be formed, but it is not now possible to tell which one is formed.

In the preparation of the phenoxozone derivative, a heavy precipitate is formed, as has already been mentioned. This consists largely of sodium chloride and sodium nitrite, but it has another constituent which is phenol-like in its character, being readily soluble in dilute alkalies and reprecipitated from them by acids. It is very much of the nature of the compound obtained by dissolving the phenoxozone derivative in strong alkali and reprecipitating with an acid. From this we might expect that the alkali present had decomposed the condensation product as rapidly as it was formed until the alkali had become so dilute that it was no longer able to effect decomposition. Since ammonium hydroxide does not decompose the hydroxydinitrophenoxozone, except very slowly, even when hot and concentrated, the idea was suggested to try to improve the yield by using an alcoholic solution of ammonia in place of

the alcoholate or hydroxide of sodium. On trying the alcoholic solution of ammonia, picramide was obtained in fair quantity, together with tarry by-products, the reaction taking place to a great extent as though the pyrogallol were not present.

As yet no definite results have been obtained in determining the character of the decomposition-product obtained by the action of strong alkali on the phenoxozone derivative, the principal difficulty being the impossibility of purifying the resulting compound. The indications are that a new compound is formed; that it possesses a strong acid character, since it is not precipitated from alkaline solutions by acetic acid, but is precipitated by hydrochloric or sulphuric acid. From these facts it is probable that the alkali has acted to split open one of the oxygen bonds, giving a trihydroxy compound having one of the hydroxy groups in the same phenyl radical which imparts to it its strong acid properties.

The hydroxyphenoxozone was reduced with tin and hydrochloric acid. When the reduction was complete and the solution cooled a white precipitate was formed which consisted of the hydrochloride of the base. This was filtered off through glass wool, dissolved in a small quantity of water, and the free base precipitated by the addition of sodium carbonate. In order to purify it, it was dissolved in hot alcohol and water added until it became turbid. On standing, fine, needle-like crystals separated out, melting at 252° to 253°. The free base is soluble in alkali, but it is apparently decomposed by it, for it is not precipitated unchanged by neutralizing with hydrochloric acid, but instead a brown, amorphous substance is thrown down. The base is soluble in alcohol and acetone, but difficultly soluble in water and the common organic solvents.

The work on the action of picryl chloride on pyrogallol was carried out by Mr. R. D. Hall, to whose skill and perseverance I am greatly indebted.

LABORATORY OF ORGANIC CHEMISTRY,
UNIV. OF WISCONSIN, May 20, 1901.

THE ACTION OF BENZOYL CHLORIDE ON AMMONIUM SULPHOCYANATE.

By Gideon Benson and H. W. Hillyer.

Benzonitrile being one of the best non-aqueous solvents for many salts, and these solutions exhibiting most interesting variations from the laws laid down for aqueous solutions, a method is desirable for its preparation, more prolific in its yield than the methods now known. While this desire has not, by the present work, been fulfilled in any complete way it is still thought best to put on record the results obtained.

The leading thought in this research was that dibenzoylthiourea might, on heating, break up into benzonitrile, hydrogen sulphide and carbon dioxide according to the equation:

$$(C_6H_5CONH)_2CS = 2C_6H_5CN + H_2S + CO_2.$$

Since ammonium sulphocyanate and thiourea are mutually changed into one another at 170°, a state of equilibrium being established, it was decided to use the former instead of the latter and study the effect of heating it with benzoyl chloride.

Ten grams of ammonium sulphocyanate were heated with 45 grams benzoyl chloride, in a retort with a reflux condenser, until no more hydrochloric acid was evolved, and the residual products distilled. The greater part of the distillate comes over between 190° to 210°, and crystallizes on cooling, forming a mass saturated with a liquid having the odor of benzonitrile. The crystals were shown to be benzoic acid, and the oil, by its boiling-point and hydrolysis to benzoic acid, was shown to be benzonitrile.

In order to study the products formed besides benzoic acid, benzonitrile, and hydrochloric acid, a new experiment was made. The mixture of benzoyl chloride and ammonium sulphocyanate was heated in a sulphuric-acid bath to 190°. The gases generated were passed through water to take up the hydrochloric acid and through lime-water to take up carbon dioxide. The gas not dissolved was found to be combustible with a blue flame and the odor of sulphur dioxide. Hydro-

gen sulphide could be detected in some cases or phases of the reaction, but was not always present even when the gas, as collected above, was combustible. The latter was found to be carbon oxysulphide.

An explanation of the above reaction was suggested by the work of Kekulé[1] in studying the action of benzoic acid on ammonium sulphocyanate. These substances, when heated together in the proportion of their molecular weights to 150° to 170°, react together, setting free carbon oxysulphide, ammonia, carbon dioxide, and carbon disulphide, and forming benzamide. The reactions involved are represented by the following equations:

$$C_6H_5COOH + NH_4CNS = C_6H_5COONH_4 + HCNS;$$
$$C_6H_5COONH_4 + HCNS = C_6H_5CONH_2 + COS + NH_3;$$
$$2COS = CO_2 + CS_2.$$

Under the influence of heat, in the presence of potassium benzoate, the amide was supposed to be dehydrated to benzonitrile.

Two series of equations, yielding the same final products, may be suggested to explain the product formed in the case now being studied:

$$C_6H_5COCl + NH_4CNS = C_6H_5COCNS + NH_4Cl;$$
$$C_6H_5COCl + NH_4Cl = C_6H_5CN + H_2O + 2HCl;$$
$$C_6H_5COCNS = C_6H_5CN + COS;$$
$$C_6H_5COCl + H_2O = C_6H_5COOH + HCl;$$

and

$$C_6H_5COCl + NH_4CNS = C_6H_5CONH_2 + HCl + HCNS;$$
$$C_6H_5COCl + HCNS = C_6H_5COCNS + HCl;$$
$$C_6H_5COCNS = C_6H_5CN + COS;$$
$$C_6H_5CONH_2 + C_6H_5COCl = C_6H_5CN + C_6H_5COOH + HCl.$$

Either of these series, when summarized, may be expressed thus:

$$3C_6H_5COCl + NH_4CNS = 2C_6H_5CN + C_6H_5COOH + 3HCl + COS.$$

[1] Ber. d. chem. Ges., 6, 113.

The second series appears, on the whole, the more probable.

To test the reaction further and to determine experimentally whether or not the amount of the products obtained by the reaction supported the hypothetical summarized equation, the reaction was carried through again and made as nearly quantitative as possible. The substances were taken in the proportions of 1 molecule of ammonium sulphocyanate to 3 molecules of benzoyl chloride.

Ammonium sulphocyanate (7.6 grams) and benzoyl chloride (42.1 grams) were brought together in a retort so placed that the neck of the retort was inclined upward. The mixture was heated to 185° to 200° until action appeared to be over or until gases were no longer evolved. The gases evolved were passed first through water to take up the hydrochloric acid, then through potassium hydroxide to take up carbon dioxide and hydrogen sulphide. Some gas not absorbed by these was collected over water. When ignited, it burned with a blue flame and yielded sulphur dioxide, but before ignition it had no odor and gave no test for hydrogen sulphide with lead acetate paper. These qualitative tests sufficiently indicate the presence of carbon oxysulphide.

When the solution of potassium hydroxide through which the gases had passed was tested with barium hydroxide, it gave evidence of the presence of a carbonate, and, when tested with lead acetate, it gave evidence of the presence of a sulphide.

The hydrochloric acid absorbed in the wash-bottle was determined as chloride and found to amount to 10.08 grams. According to the theory the quantity used should have yielded 10.95 grams.

The reaction-product in the retort was then distilled over a free flame. All distilled over except 2.6 grams of a tarry residue and a small amount of yellow crystals in the neck of the retort.

The distillate was reddish-brown and crystallized on cooling. The first distillate was redistilled. About half passed over below 200°. The residue was nearly colorless. Both portions were treated with sodium carbonate and shaken out

with ether. The ethereal solutions were dried and the ether evaporated. There was a residue containing 15 grams of pure benzonitrile passing over between 190° to 192° and leaving a black, oily mass, containing benzonitrile and benzoic acid. These were separated by sodium carbonate and extracted with ether, and in this way 1 gram more of benzonitrile was obtained.

The sodium carbonate solutions were acidified with hydrochloric acid, and the benzoic acid which was precipitated was filtered off, and after being dried weighed 11.25 grams. Since benzoic acid is soluble in water to the extent of 3 parts per thousand and the total wash-water was 920 cc. we should add to the amount weighed 2.75 grams, making in all 14 grams. Theoretically, the amount of benzonitrile obtained would be 20.6 grams and of benzoic acid 12.2 grams.

The weight of nitrile obtained by the experiment, however, was 16 grams, or 78 per cent of the theoretical, while the weight of acid was 14 grams, or 115 per cent of the theoretical. These variations can easily be accounted for by the presence of a very small amount of moisture in the ammonium sulphocyanate. The residues must also be considered. From 42.1 grams benzoyl chloride are obtained :

	Theoretical. Grams.	Found. Grams.
Benzoic acid	12.2	14.00
Hydrochloric acid	10.97	10.08
Benzonitrile	20.97	16.00

By this method a yield of 38 per cent of the benzoyl chloride used was obtained as benzonitrile.

The three methods mentioned in the literature which give the product are those of Fehling,[1] Letts,[2] and Henry.[3]

Fehling made benzonitrile by heating ammonium benzoate. The yield was 50 per cent of the benzoic acid used, but the process is a very slow one, requiring five days to give 6 ounces of product.

Letts, by heating 2 molecules of benzoic acid with 1 mole-

[1] Ann. Chem. (Liebig), **49**, 92.
[2] Ber. d. chem. Ges., **5**, 675.
[3] *Ibid.*, **2**, 307.

cule of potassium sulphocyanate obtained hydrogen sulphide, carbon dioxide, and benzonitrile, the yield of the last being 34 per cent of the benzoic acid used, or 80 per cent of the amount predicted by the equations:

$$C_6H_5COOH + KCNS = C_6H_5COOK + HCNS;$$
$$C_6H_5COOH + HCNS = C_6H_5CONH_2 + COS;$$
$$C_6H_5CONH_2 = C_6H_5CN + H_2O.$$

Henry found that, when benzamide and phosphorus pentasulphide were distilled together, hydrogen sulphide and benzonitrile are obtained. By this method about 42 per cent of the benzamide used was obtained in the form of pure nitrile.

Taking into account the price and availability of the initial substances in the four methods there seems to be no great advantage in favor of either one.

LABORATORY OF ORGANIC CHEMISTRY,
UNIV. OF WISCONSIN, May 24, 1901.

THE REDUCTION OF COPPER BY SOLUTIONS OF FERROUS SALTS.

BY H. C. BIDDLE.

The genesis of the great deposits of native copper is a subject which has invited considerable attention. The commonly accepted theory that the copper has been deposited from its compounds by solutions of ferrous salts is based on the close relation between the reduced metal and the ferric oxide contained in the associated minerals.[1] It is consequently of interest to determine experimentally under what conditions such reduction may occur. Some investigation has already been conducted in this direction.

As early as 1861 Knop succeeded in forming cuprous hydroxide by treating a mixture of cupric and ferrous sulphates with alkaline carbonate.[2] In one instance he speaks of obtaining traces of copper. In 1864 Wibel repeated Knop's experiments,[3] but was unable to verify the latter's statement re-

[1] Raphael Pumpelly: Am. J. Sci., **2**, 353 (1871); R. D. Irving: Mon. U. S. Geol. Surv., No. 5, p. 420 (1883).

[2] A. Knop: N. Jahrb. für Min., (1861), p. 513.

[3] Ferd. Wibel: "Das Gediegen-Kupfer und das Rothkupfererz," (1864), p. 20.

garding the reduction to metallic copper. When, however, a mixture of ferrous and cupric hydroxides, formed by adding potassium hydroxide to a solution of the sulphates, was heated to 210° C., traces of copper were obtained. Solutions of the sulphates and coarsely powdered wollastonite, subjected to the same treatment, yielded a like result. The separation of metal, however, was slight and the part played by the ferrous hydroxide in the reduction was, at the time, somewhat questioned.

In 1867 Braun observed the partial deposition of copper from a mixture of ferrous and cupric salts when these were dissolved in large excess of ammonium carbonate.[1] The same year Weith secured a ready reduction in the presence of tartaric acid.[2]

He failed to note, however, that under the same conditions the organic acid itself will slowly reduce the copper salts. A mixture of calcium hydroxide with a solution of ferrous and cupric sulphates, was allowed to stand for several weeks. The precipitate thus obtained, when treated with acetic acid, left a residue of cuprous oxide and copper. Strangely enough, Weith overlooked the fact that cuprous oxide with acetic acid yields cupric acetate and metallic copper. In 1869 Hunt[3] stated that copper could be obtained by the action of cupric chloride on freshly precipitated ferrous hydroxide, or carbonate. Nothing is given, however, to indicate that the metal was actually detected by isolating it from ferric hydroxide precipitated along with it.

The deposition of copper by solutions of ferrous salts is a reversible reaction governed by the ordinary laws of chemical equilibrium.

It is to Arrhenius largely that we owe the view that certain substances in solution are more or less dissociated into electrically charged parts, or ions. This theory has proved of the highest value in affording an insight into the principles of chemical reactions. Different substances differ much in their tendency to pass into the ionic form, and this ten-

[1] E. Braun: Ztschr. Chem., (1867), p. 569.
[2] W. Weith: *Ibid.*, (1867), p. 623.
[3] Sterry Hunt: Compt. rend., (1869), p. 1357.

dency is greatly influenced by external conditions, particularly by the nature of the solvent. The chief source of ions is the dissociation of electrically neutral molecules such as occurs in the aqueous solutions of salts, acids, and bases. They may further be formed from electrically neutral substances which enter the ionic condition by partially, or wholly, appropriating the electric charge of ions already present.[1]

As an example of this mode of formation may be mentioned the reduction of ferric salts by the action of metallic iron :

$$2FeCl_3 + Fe = 3FeCl_2.$$

The solution of metallic copper in ferric chloride is an action of the same nature :

$$Cu + 2FeCl_3 = CuCl_2 + 2FeCl_2.$$

As is seen, the deposition of copper by a ferrous salt would be the reverse of this last reaction.

The conditions under which such reduction should occur may be readily determined. In a system which contains a solution of iron and cupric salts in contact with metallic copper, and in which the several constituents have attained a constant value, a condition of equilibrium subsists, on the one hand, between ferric, cuprous, ferrous, and cupric ions

$$(Fe''' + Cu' \rightleftarrows Fe'' + Cu''),$$

and, on the other hand, between ferric, ferrous, and cuprous ions, and the active mass of the metallic copper

$$(Cu + Fe''' \rightleftarrows Fe'' + Cu').$$

If a, b, c, d, respectively, represent the active masses of the ions in the first instance, an equation of equilibrium may be thus formulated : $\frac{a \cdot b}{c \cdot d} = K$.[2] The active mass of the copper is of constant value, hence in the second instance, retaining the same letters, we have the expression $\frac{a}{b \cdot c} = K'$.

[1] F. W. Küster : Ztschr. Elektrochem., **4**, 105.
[2] W. Nernst : "Theoret. Chem.," p. 358.

The precipitation of copper would then be favored by increasing the concentration of ferrous, cuprous, and cupric ions and by decreasing that of the ferric ions.

The deposition of the metal, consequently, should depend on the relative active masses of the ions present.

This assumption is fully sustained by the experimental evidence which follows:

The precipitation of metallic copper by solutions of ferrous salts is a reversible action, whose direction in any case is determined by the relative concentration of the ferrous, ferric, and copper (cuprous and cupric) ions.

(*a*) In a solution containing an appreciable quantity of ferric ions, or in which these would be formed in the course of the reaction, metallic copper will not be deposited.

This is shown in the inability of ferrous chloride, or sulphate, to reduce corresponding copper salts, even though the mixed solutions stand for an indefinite period. This inaction is, indeed, to be expected when we consider that solutions of ferric salts, as the sulphate and chloride, easily dissolve metallic copper with the formation of a cupric salt.

From this it is readily understood why Wibel[1] obtained no reduction of the copper salts on heating the mixed sulphates together to 210° C. in solution.

(*b*) In a solution containing few ferric ions, and in which the reaction does not result in their appreciable increase, a sufficient concentration of ferrous and copper ions will result in the deposition of metallic copper.

The tendency of ferrous to reduce copper salts is shown in the precipitation of cuprous sulphocyanate by the action of the ammonium salt on a solution of ferrous and cupric chlorides. The same tendency appears in the formation of cuprous chloride on treating cupric oxide with a solution of ferrous chloride.[2] From an emulsion of ferrous and cupric hydroxides, after long standing, crystals of cuprous oxide can be separated. That further reduction is largely determined by the concentration of the cupric and ferrous ions, appears prob-

[1] "Das Gediegen-Kupfer und das Rothkupfererz," p. 20.

[2] Sterry Hunt: *Loc. cit.*

able from the action of ammonium carbonate on a solution of ferrous and cupric chloride.[1]

The precipitate first formed on adding the carbonate to the mixed chlorides dissolves in an excess of the precipitant to a yellow liquid, from which, on standing twenty-four hours, a slight but brilliant mirror of metallic copper is deposited on the walls of the vessel.

The influence of the concentration of the ions on the reduction of copper is clearly shown in the behavior of the mixed carbonates under varying conditions.

When a solution of cupric and ferrous chlorides (1 mol. $CuCl_2$: 2 mol. $FeCl_2$) is added to a considerable excess of sodium carbonate, a greenish precipitate of the carbonates is obtained, which undergoes but slight change on standing. Such a solution, indeed, would naturally little favor the separation of metallic copper, since the highly ionized alkaline carbonate would greatly decrease the active masses of the ferrous and ferric ions.

If the alkaline carbonate employed is only slightly in excess of that required to precipitate the copper and iron salts, the concentration of the carbonic acid ions will be greatly diminished. Under these more favorable conditions reduction slowly takes place with loss of carbon dioxide. The carbonates gradually change to a brick-red precipitate containing metallic copper and basic ferric carbonate.

As is well known, the acid ferrous and cupric carbonates are more soluble than the corresponding normal or basic salts of these metals. The influence of this greater solubility is shown in the precipitation of small amounts of copper even in the presence of a large excess of alkaline bicarbonates. If the metallic chlorides are added to a saturated solution of acid potassium carbonate and the mixture allowed to stand for twenty-four hours, a slight film of metallic copper, mixed with basic ferric carbonate, is deposited on the walls of the vessel.

The solubility of the acid carbonates of iron and copper is largely increased under pressure.[2] The greater concentration

[1] R. Braun: *Loc. cit.*

[2] R. Wagner: Ztschr. anal. Chem., 6, 167.

of the metallic ions thus obtained produces a ready reduction of copper even in the presence of concentrated solutions of the acid alkaline carbonates.

A tube containing a solution of ferrous and cupric chlorides is placed in a thick-walled flask holding a saturated solution of potassium bicarbonate. The flask is then filled with carbon dioxide, tightly sealed, and the contents of the tube mixed with the alkaline bicarbonate. The precipitate formed gradually loses carbonic acid, finally assuming the brick-red color already noted. The supernatant ruddy liquid owes its color to the presence of some basic ferric carbonate, which is deposited when the solution is warmed, as ferric hydroxide. The precipitate contains finely divided copper, which cannot readily be freed from the intimately associated ferric iron by treatment with hydrochloric acid, because of the solvent action of ferric chloride, but on digesting the original mixture a short time a coagulum is usually formed, from which, by repeated agitation with water, the heavier metal is separated.

The copper thus obtained is of characteristic appearance, is insoluble in hydrochloric acid, but soluble in nitric, the solution showing the presence of copper and absence of iron.

The reduction of copper from the cuprous condition may be effected in the same manner as from the cupric. This is readily shown by substituting for the cupric salt, in the above reaction, cuprous chloride dissolved in a solution of sodium chloride. From one gram of cuprous chloride more than half of the metal can thus be easily isolated as pure copper, free from ferric iron.

UNIVERSITY OF CHICAGO.

OBITUARY.

WALDRON SHAPLEIGH.

On the 30th of August died Mr. Waldron Shapleigh. Mr. Shapleigh had been connected with the Welsbach Light Company from its beginning, as its chemist, and was very well known in scientific circles as perhaps the best authority living on the properties of rare earths.

Mr. Shapleigh began his life of manly independence at an unusually early age. He decided against a college course, and studied chemistry under the late Professor Williams. At the age of nineteen he was made Superintendent of the Blair County, Pa., Zinc Works, and a year later accepted a position as Instructor of Chemistry at Lehigh University. He remained there several years, at the last filling the place and receiving the salary of Professor Wetherill, after the latter's death. Determining to enter a different field of chemistry, Mr. Shapleigh severed his connection with the University and went to France to study the beet-root sugar industry. He remained there nearly two years, and upon his return was engaged as chemist by the Kings County Sugar Refinery, New York, then engaged in the manufacture of glucose. Mr. Shapleigh remained with this company for ten years, until its dissolution. He next entered the Welsbach Company, when it was founded as an industry, and it is through his connection with it that he became so widely known in scientific circles, both in Europe and America.

Mr. Shapleigh was chosen as one of the judges of awards in the chemical section at the Columbian Fair in 1893, and his exhibitions of rare earths at different expositions have always received medals.

Mr. Shapleigh was a man of unusual character; in an age of greed to be rich he kept before him a certain simply strenuous ideal of high old-fashioned honor from which he never departed. He was a rare combination of strength and gentleness, impressing every one who knew him with deep respect. By those friends who could pierce the armor of shy reserve which hedged him about, he was deeply loved and deeply lamented. He leaves a widow, a son, and a daughter.—*N. Y. Evening Post.*

NOTE.

The Dissociating Power of Hydrogen Sulphide.

In view of the analogous behavior, in many respects, of oxygen and sulphur, it would seem quite probable that hydrogen sulphide in the liquid state should possess, in common with water, the property of ionizing substances in solution.

It is more difficult to experiment with hydrogen sulphide than with liquid ammonia, which has recently been so thoroughly tested in this respect, on account of the difficulty of reducing it to the liquid state.

The liquefaction of sufficient gas to serve as an electrolyte was accomplished at room temperature in a Pictet compression apparatus, some grains of potassium chloride having been previously placed in the tube. The column of mercury within the tube served as one electrode, and a platinum wire, sealed into the top of the tube, as the other.

The salt readily went into solution when the liquid collected in the tube, but, on making electric connections, there did not appear to be any conduction.

The liquid exerted considerable action upon the mercury surface, and, fearing that this coating of sulphide might form an insulating layer, two platinum electrodes were used, but with a negative result again. The galvanometer in the circuit, a fairly sensitive one of the Wheatstone type, did not show any deflection, even when a battery of 40 volts was used.

An attempt to use an iron wire as electrode showed a most vigorous chemical action upon the iron. WM. T. SKILLING.

UNIV. OF CALIFORNIA,
July 4, 1901.

REVIEWS.

LECTURES ON THE HISTORY OF THE DEVELOPMENT OF CHEMISTRY SINCE THE TIME OF LAVOISIER. By DR. A. LADENBURG. Translated from the second German edition by LEONARD DOBBIN, PH.D., with additions and corrections by the author. Edinburgh: Published by the Alembic Club. Edinburgh Agent: William F. Clay. pp. xvi + 373. Price, 6s. 6d.

There are two views of history. One regards it merely as a record of events. The other regards every event as closely dependent on what has gone before and closely related to what follows, and concerns itself with tracing the sequence which always exists. It is evidently this latter view which is dominant with Professor Ladenburg as he writes. The first German edition of the book was published thirty years ago; the second, and last, fifteen years ago, but an additional chapter has been prepared for use in this translation, bringing the material very closely down to date.

The picture which is given of the growth of chemical science from the time of Lavoisier down through the first two-thirds of the nineteenth century is very clear and satisfactory. Up to, and including the development of structural organic chemistry, it has been possible to bring out the various factors which have contributed to the development of our knowledge in bold relief and proper relation. The author has performed a very difficult task in a most excellent manner.

The historian of the progress of the last thirty years meets with a two-fold difficulty. The science has become vastly more complex, and the number of workers is greatly increased, giving a wealth of material that no one can grasp in its entirety. And the period is so close to our own time that it is impossible to separate the permanent from that which is ephemeral. For this reason the chapters dealing with this period consist chiefly of a series of very brief statements about a multitude of new discoveries, and that clear, logical arrangement, which characterizes the earlier portions of the book, has been impossible.

The value of the book is greatly increased by more than a thousand references to original papers. These will make it easy, for those who wish, to follow in greater detail the topics which are discussed.

Only very rarely are to be found sentences written fifteen or thirty years ago which need some change in the light of present knowledge. No one would now contend, as is implied on page 270, that the unsaturated acids studied by Fittig in the seventies contain bivalent carbon atoms. And it is, perhaps, too much to ask that Ladenburg should give the facts which demonstrate that his prism formula for benzene is false.

The translation is excellent throughout. W. A. N.

PRACTICAL ELECTROCHEMISTRY. By BERTRAM BLOUNT. Westminster: Archibald, Constable & Co., Ltd. New York: The Macmillan Co. 1901. pp. xii + 374. Price 15s.

This book consists, chiefly, of a description of practical processes which are in actual commercial use. Only the first thirty pages are given to a discussion of general principles. While a fairly clear general statement of the theory of solutions is given, the attitude of the author in the matter is indicated by the following sentences: "This conception is a mode of thought and not an objective reality, and may eventually be replaced by a hypothesis involving fewer and less sweeping assumptions. * * * * Fortunately all practical applications of electrolysis can be satisfactorily considered without having recourse to this hypothesis, and the practician who is equipped with a sound knowledge of the principles of chemistry and electricity can grapple successfully with any problem in electrolysis which is likely to present itself, irrespective of the precise explanation which may be at the moment most agreeable with the teachings of the ionic hypothesis." Such a statement may be essentially true so far as the present development of technical electrochemistry is concerned, but that it will long remain true, no one acquainted with the achieve-

ments of the theory along purely scientific lines, will believe.

The technical processes considered in the book are: Winning and refining of metals by electrolysis in aqueous and in igneous solutions; winning and refining metals and their alloys in the electric furnace—carbides, borides, and silicides; electro-deposition; alkali, chlorine, and their products; electrolytic manufacture of organic compounds and fine chemicals; and power. What the book lacks from the theoretical standpoint is very largely compensated by the careful descriptions given of methods in actual use, with details of the materials and products obtained, and of the voltages and energy required.

The value of the book would be increased by the introduction of a few tables of physical constants. W. A. N.

THE ELEMENTARY PRINCIPLES OF CHEMISTRY. By A. V. E. YOUNG, Professor of Chemistry in Northwestern University. New York: D. Appleton & Co. 1901. Part I: pp. 252 + xiv; Part II: pp. 106. SUGGESTIONS TO TEACHERS DESIGNED TO ACCOMPANY THE ELEMENTARY PRINCIPLES OF CHEMISTRY. Pp. 48.

This is a scholarly book. The author is a strong advocate of the value of the quantitative method in an elementary course and in preparing his book he has had this constantly in mind. He says: "The quantitative method aims to bring the student into direct contact, so to speak, with the relations of quantity as well as with those of quality. It most distinctly does not aim to present the systematic methods of quantitative analysis. No more does it propose that the pupil shall prove to his own mind the laws of quantity. Such laws are inductions from a great many observations, and the student should be carefully guarded against the idea that his experiments are to prove them, even to his own conviction. His experimentation is simply to aid him by direct observation and by guided thought to get a clear notion of the content and meaning of laws."

The first seven chapters (89 pages) of the book have to deal with the following subjects:

I. Matter, Energy, Substances, Chemical Properties, Physical Properties.

II. The Fundamental Quantitative Laws of Chemical Changes.

III. Combining Weights, Notation, Equations, Stoichiometry, Nomenclature.

IV. Relation between Volume, Pressure, and Temperature of Gases.

V. The Relation between Equivalent and Combining Weights and Certain Specific Properties.

VI. Method of Determining Equivalent and Combining Weights of Elements and Formulas of Compounds.

VII. The Atomic Theory.

As will be seen, the student has been occupied up to this time with the study of the great fundamental laws of chemistry and some of its most important theories, and his laboratory work has had for its object the illustration and emphasizing of these laws and theories. Now in Chapter VIII, which deals with the "Relation between the Properties of the Elements in General and their Combining Weights," he begins a systematic, though necessarily brief, study of the important elements and their principal compounds. This chapter occupies about 150 pages. It is clearly written and the material is wisely selected. The book deserves a careful examination. Whether it is better adapted to the needs of the beginner than other books now in use can only be determined by experiment.

THE HISTORY OF THE DEVELOPMENT OF THE MANUFACTURE OF INDIGO. By H. BRUNCK, PH.D.

This is a good English translation of the remarkable address of H. Brunck, Managing Director of the Badische Anilin- und Soda-Fabrik, delivered October 20, 1900, on the occasion of the Dedication of the Hofmann Memorial in Berlin, erected in honor of A. W. von Hofmann by the chemists of all nations. It has been prepared and presented to their friends and patrons by Messrs. Kuttroff, Pickhardt & Co., of New York. As the address was published in full in the *Berichte* and has been republished elsewhere, it is not necessary to go into detail in regard to it here. Suffice it to say that in the opinion of the present writer it is one of the most interesting addresses ever presented to chemists. This beautifully prepared pamphlet gives it a worthy setting. Every chemist, whether "inorganic," "organic," "physical," "analytical," "industrial," or just plain chemist, will do well not only to read the address but to study it. I. R.

AN INTRODUCTION TO THE STUDY OF CHEMISTRY. By IRA REMSEN, Professor of Chemistry in the Johns Hopkins University. Sixth edition. Revised and enlarged. New York: Henry Holt and Company. 1901. pp. 460 + xxii.

The preface will serve to give an idea of the general character of this revised edition: "Since the appearance of the last edition of this book many important discoveries have been made in chemistry. In preparing the new edition the author has endeavored to include all discoveries that come within the scope of the book, and it is believed that nothing that could

fairly be looked for in a book of this size has been omitted. The experiments have not been essentially changed. The question whether it is advisable to introduce a larger number of quantitative experiments was fully considered. The conclusion reached was that in the time generally available, it would be impossible properly to perform a larger number of such experiments than is described in the earlier editions. That has been our experience in our first year's course, and it has been the experience of many teachers who have kindly given the author the benefit of their advice.

"Some account of the new theory of solutions is given, and its application to the explanation of reactions that take place in water solutions receives consideration. It would, of course, be an easy matter to go further into the subject, but it does not seem to the author wise to do so in the earliest stages of the study of chemistry."

A TEXT-BOOK OF URINE ANALYSIS FOR STUDENTS AND PRACTITIONERS OF MEDICINE. By JOHN H. LONG, M.S., Sc.D. With numerous illustrations. Easton, Pa.: THE Chemical Publishing Co. 1900. pp. vi + 249. Price $1.50.

The experience of the author, both as a professor in a medical school and as a practical analyst, as well as his own researches in the field of urine analysis, have given him an unusually thorough preparation for the writing of a book on this subject. The result is a work excellently adapted for practical use. While the book is comprehensive in its scope, giving a considerable number of qualitative tests and of quantitative methods for determining the more important constituents of the urine, the claim of the author that methods of doubtful utility are consistently excluded is well sustained.

Not only is the book well written from the chemical standpoint, but clear statements of the clinical significance of the various substances discussed supply the need of the medical practitioner. Careful directions for the microscopical examination of sediments are included, and these are supplemented by a sufficient number of figures illustrating the substances to be looked for.

An appendix gives the necessary tables, directions for the preparation of reagents, and an excellent tabular statement of the clinical significance of the results of analysis, and also, in detail, the character of the urine to be expected in eight important diseases. W. A. N.